



Towards improving H₂S catalytic oxidation on porous carbon materials at room temperature: A review of governing and influencing factors, recent advances, mechanisms and perspectives

Chao Yang^a, Yeshuang Wang^b, Meisheng Liang^a, Zhelin Su^b, Xuan Liu^b, Huiling Fan^{b,*},
Teresa J. Bandoz^{c,*}

^a College of Environmental Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China

^b State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China

^c Department of Chemistry and Biochemistry, The City College of New York, 160 Convent Avenue, New York, NY 10031, United States

ARTICLE INFO

Keywords:

Hydrogen sulfide dissociation
Porous carbon materials
Catalytic oxidation
Surface chemistry
Oxygen activation

ABSTRACT

Given that H₂S detrimentally affects various aspects of human life including an environment, health, industrial infrastructure and catalytic processes, its removal from various gas streams is of paramount importance. As the most promising alternative, room temperature H₂S catalytic oxidation on carbon-based materials attracted extensive attentions owing to its low costs, high efficiency and a possibility of sulfur recovery. These catalysts' features such as a high surface area, adjustable porosity, enriched surface chemistry, easy surface modification and good conductivity, bring advantage to the desulfurization processes. This review focuses on ambient H₂S catalytic oxidation on carbonaceous materials, highlights the importance of various factors governing and influencing the performance and critically analyzes recent findings. It also comprehensively summarizes the results collected on various carbonaceous materials and systematically outlines plausible catalytic oxidation mechanisms. Based on the collected results, some challenges needed to be addressed to further advance the field are pointed out.

1. Introduction

Hydrogen sulfide (H₂S) is a colorless gas of rotten eggs-like odor. It is extremely toxic, corrosive, flammable (ignition temperature of 250 °C) and explosive (4.5–46 % in air) [1,2]. The diverse sources of H₂S can be divided into those of natural and anthropogenic origins. H₂S naturally occurs in various concentrations in industrial waste gases and hydrocarbon sources such as crude petroleum, natural gas, and biogas [3]. An anaerobic digestion and volcano eruptions also contribute to its generation. The anthropogenic sources mainly originate from coal/biomass gasification and refinery processes of hydro-desulfurization, hydro-refining and some crack operations, and also from a sewerage treatment [4,5]. Fig. 1 lists the typical concentrations of H₂S in various gas streams. Depending on their origin, the concentrations of H₂S in these gases show a broad range of values [6–14]. Nonetheless, H₂S in these gases, even in small amounts, can corrode pipelines and equipment, resulting in a failure of transportation and operation systems. More importantly, H₂S can deactivate noble metals or/and metal oxides

catalysts used for downstream catalytic processes, extremely increasing the operation costs of an industrial production [15]. It cannot be ignored that H₂S is also hazardous to human health and it can be readily perceived by humans at the concentrations as small as 0.01–0.3 ppm [2, 16]. Moreover, H₂S can be oxidized into SO₂, poisonous gas that can trigger acid rains, deteriorating the ecological balance of Earth.

In order to remove H₂S from a gas phase, various desulfurization processes have been established, including liquid-phase absorption [3, 17,18], solid-phase adsorption [15,16,19,20], membrane separation [21–24], biological processing [25–27], and catalytic oxidation [28–31]. Among them, the latter is considered as the most promising strategy. It is because its major product is elemental S, and the method is cost-feasible. The Claus process is a well-developed technology to recover sulfur through H₂S oxidation. In its mechanism, some H₂S is first oxidized into SO₂ by O₂ and then the remained H₂S reacts with SO₂ to form elemental S [4,32,33]. This process requests a high temperature at above 400 °C and is suitable for treating high concentrations of H₂S (over 20 vol%) [4]. Owing to the thermodynamic limitations, ~5 vol%

* Corresponding authors.

E-mail addresses: fanhuiling@tyut.edu.cn (H. Fan), tbandosz@ccny.cuny.edu (T.J. Bandoz).

<https://doi.org/10.1016/j.apcatb.2022.122133>

Received 7 August 2022; Received in revised form 28 October 2022; Accepted 29 October 2022

Available online 2 November 2022

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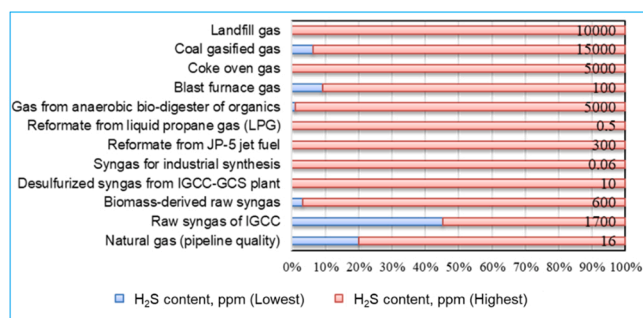


Fig. 1. The typical concentrations of H₂S in various gas streams.

of H₂S in feed gas is left as a residual [34]. In order to further improve the sulfur recovery efficiency, a Super-Claus process was developed with the sulfur recovery efficiency of 95 %–99.5 vol% [28], however still a residual ~0.5–4 vol% of H₂S in the feed gas remains to be addressed. In traditional industries a wet catalytic oxidation process is adapted to lower H₂S concentrations reaching 20 vol%. The common catalysts are arsenic, vanadium and chelated iron-species [35,36]. H₂S is first absorbed by alkaline solvents and S²⁻ or HS⁻ formed are subsequently catalytically oxidized into elemental sulfur in a liquid phase at room temperature. However, this process needs huge equipment and complex operations, rising the costs of installations. Moreover, the treatment of wastewater generated in the wet catalytic oxidation methods remarkably increases desulfurization costs. H₂S selective catalytic oxidation is considered as a promising strategy to address H₂S concentrations lower than 5 vol% [37–43]. Owing to the high H₂S removal efficiency and advantage of addressing low H₂S concentrations, it has been significantly advanced after a recent development of single atom catalysts [31, 34,44]. This process involves a direct oxidation of H₂S into elemental sulfur by oxygen, and occurs without thermodynamic limitations [28]. The recent advances in H₂S selective catalytic oxidation have been reviewed in the previous works [28,45] and they are out scope of this review.

Room temperature H₂S catalytic oxidation focuses on a low H₂S concentration and it attracted an increasing attention of scientists and engineers due to its facile operation and low costs. In this process the products of H₂S oxidation are deposited in the pore system of catalysts, gradually clogging pores and deactivating catalytic sites. Porous carbon materials are widely used as catalysts for H₂S room temperature catalytic oxidation, following their advantages of a large surface area, adjustable porosity, enriched surface chemistry, easiness of surface modifications, conductive character and abundant carbon precursors' sources [46]. On the other hand, on metal oxides relatively high temperatures are needed to advance this process. The extended surface area of carbons (not comparable to those of metal oxides) results in exposing a large quantity of sites active in the desulfurization process. Moreover, a broad range of carbon production/synthesis and surface modifications routes brings various paths for a rational design of efficient catalysts. Led by marked developments in carbon materials' science and technology, recent years have brought great advances in H₂S catalytic oxidation on porous carbon materials at room temperature.

Based on the mentioned above needs for the efficient room temperature gas phase desulfurization processes and catalysts, herein we give an overview on H₂S catalytic oxidation on the carbonaceous materials by systematically analyzing the factors governing H₂S catalytic oxidation on various modified carbon catalysts. We address oxygen activation sites, an alkaline environment and redox activity of iron containing species, and discuss the influence of moisture in feed gas, heterogeneity of pore sizes, oxygen groups incorporated to the carbon surface, composition of challenge gas, carbon conductivity and speciation of the products on the H₂S removal performance during desulfurization. In the second part, recent advances (past decade) in room temperature H₂S

catalytic oxidation on various porous carbonaceous materials, such as activated carbons, mesoporous carbons, carbon nanotubes, graphite/graphene oxides, and carbon fibers, along with calculation results supporting experiments are addressed. Lastly, based on the collected results, plausible H₂S catalytic oxidation mechanisms are outlined taking into account the interplay of the factors. Future perspectives are also included.

This review is organized in such a way that in the identification of the factors governing or influencing H₂S oxidation at room temperature on the carbon materials, we focus on the first works reporting them and then on a direct advancement in an identification of a particular factor. Therefore, the first reported observations/ correlations might not appear as very strong since they relied on the specific state of science development at that time. Nevertheless, these findings are valid, as discussed in the second part of this review, where reports on a high catalytic activity are included, and where the factors addressed in the first parts were used by researchers to explain a measured performance. In our opinion these small but important initial steps built the foundation for the further development in this field and they deserve a direct recognition. We intend to clearly indicate that these findings were used by other researchers as bases for further advancements and the strong correlations are in fact visible in recent advances addressed in the second part of this review. This review, by its both, comprehensive and critical contents, is expected to provide an inspiration and guidance for researchers from academic and industrial communities to develop most efficient H₂S removal catalysts working at room temperature with a minimum energy input. Both, gas phase desulfurization and limited energy consumption are important to minimize detrimental effects of fossil fuels on our environment.

2. Factors governing H₂S catalytic oxidation on various modified carbons

For a catalytic reaction, it is of great importance to well-recognize active sites and a structure-activity relationship. This understanding is critical to develop reaction mechanisms and then to rationally design high-performance heterogeneous catalysts. In terms of H₂S catalytic oxidation on carbonaceous materials at room temperature, there is a general consensus that O₂ activation, H₂S dissociation, and a redox electron transfer are critical steps governing this catalytic process. In the subsections below we have addressed the proposed oxygen activation sites and specific chemistry advancing H₂S dissociation to HS⁻ ions on various carbon-based catalysts. Specific engagement paths are discussed in depth. We limit the discussion of the examples to those first reported and thus creating foundation for further research, although the same or slightly modified catalytic paths are addressed in many following works in the literature. In addition, H₂S catalytic oxidation on carbon catalysts modified with Fe-containing species is discussed owing to their redox activity and a synergistic effect advancing this process.

2.1. Oxygen activation sites

Owing to the stability of triple state with spin-parallelized electrons, the molecular oxygen (O₂) needs to be activated into active oxygen species such as dissociatively adsorbed oxygen (O*) or/and superoxide radical (O₂•⁻), and then it can participate in H₂S oxidation. At the current stage of knowledge, ultramicropores (pore sizes below 0.7 nm), carbon defects, doped nitrogen atoms and copper species have been indicated as specific sites contributing to O₂ activation on various carbon-based catalysts. Their oxygen activation mechanisms markedly differ depending on the nature of active sites involved in this process.

2.1.1. Ultramicropores and defects in a carbon matrix

Owing to the high surface energy and adsorption potential, ultramicropores have been empirically considered as active centers for oxygen activation [47]. However, there was no direct evidence supporting

this hypothesis and the corresponding activation mechanism has been puzzled. This status quo was changed by Pan et al. [48], who demonstrated that the ultramicropores with sizes at around 0.4 nm can activate O_2 into the superoxide radical ($O_2^{\bullet-}$) at room temperature. The authors uncovered the activation mechanism using a radical detection method combined with DFT calculations. They suggested that the oxygen activation process involves strong adsorption of O_2 in the ultramicropores and a transfer of electrons from the carbon matrix to the adsorbed O_2 , forming $O_2^{\bullet-}$ radical. The mechanism is presented in Fig. 2a, which visualizes a closed arrangement of at least two graphene walls, resulting in the formation of slit-shape micropores commonly existed in the carbon matrix. In these ultramicropores with sizes of 0.4 nm, which is close to the size of the O_2 molecule, the overlapping of the adsorption potential of both walls promotes $O=O$ bond distortion. Then the conductive sp^2 -conjugated graphene walls having plenty of π^* electrons transfer one π^* electron to O_2 forming $O_2^{\bullet-}$. It was suggested that this process is enhanced by edge sites, topological defects, and doped heteroatoms (such as O, N atoms) present in a graphene lattice.

Using the DFT calculations, Pan et al. [48] also explored the effect of different ultramicropore sizes, ranging from 0.36 to 0.45 nm with a 0.01 nm increase, on O_2 activation. They found that when the pore diameter is less than 0.42 nm, adsorbed O_2 obtains enough electrons from the carbon matrix forming $O_2^{\bullet-}$. This process ceases in the pore diameter ≥ 0.44 nm, owing to the dramatic decrease in the quantity of the Bader charge transfer. This result indicated the need of both, very small ultramicropores and an electron transfer for O_2 activation. DFT results also revealed that the sizes of ultramicropores markedly influence the bond length of O_2 and its adsorption energy, as seen in Fig. 2(b, c), which affect O_2 activation. The authors also calculated the Gibbs free

energy before and after O_2 adsorption in the ultramicropores. The results suggested that O_2 adsorption is thermodynamically favorable in pores with a diameter higher than 0.43 nm, but the effect was opposite when the pore diameter was less than 0.39 nm (Fig. 2c). Interestingly, the calculated Gibbs free energy was almost zero in pores between 0.40 and 0.42 nm, which suggested the unrestricted adsorption of the O_2 molecules in these ultramicropores and their easy desorption from them. This process guarantees the continuous supplement of $O_2^{\bullet-}$ for H_2S oxidation in aerobic conditions. Certainly, the kinetic diameter of the oxygen molecule of 0.32 nm must have played an important role in the accessibility of pores of these sizes [49].

Defects, such as a pentagon-heptagon pair and edge plane defects, inevitably exist in carbon matrices. Their presence significantly modifies the electronic structure of carbons [50,51], and thus grants these defects' contribution as the sites for oxygen activation. Chen et al. [52] proposed that the edge (or defects) carbon atoms readily capture molecular O_2 and dissociate it into adsorbed oxygen (O^*). It was suggested that this was owing to an increased electron cloud density of these defects. A different activation mechanism was also found by Pan et al. [48], who indicated that the edge carbon defects promote the charge transfer from edged carbon atoms to molecular O_2 , which allows the formation of $O_2^{\bullet-}$. This process is easier than that on a basic graphene plane. Obviously, although researchers reached an agreement on the carbon defects as oxygen activators, the activation mechanisms are still controversial and in future more efforts need to be focused on this important aspect of H_2S catalytic oxidation on the carbon-based materials.

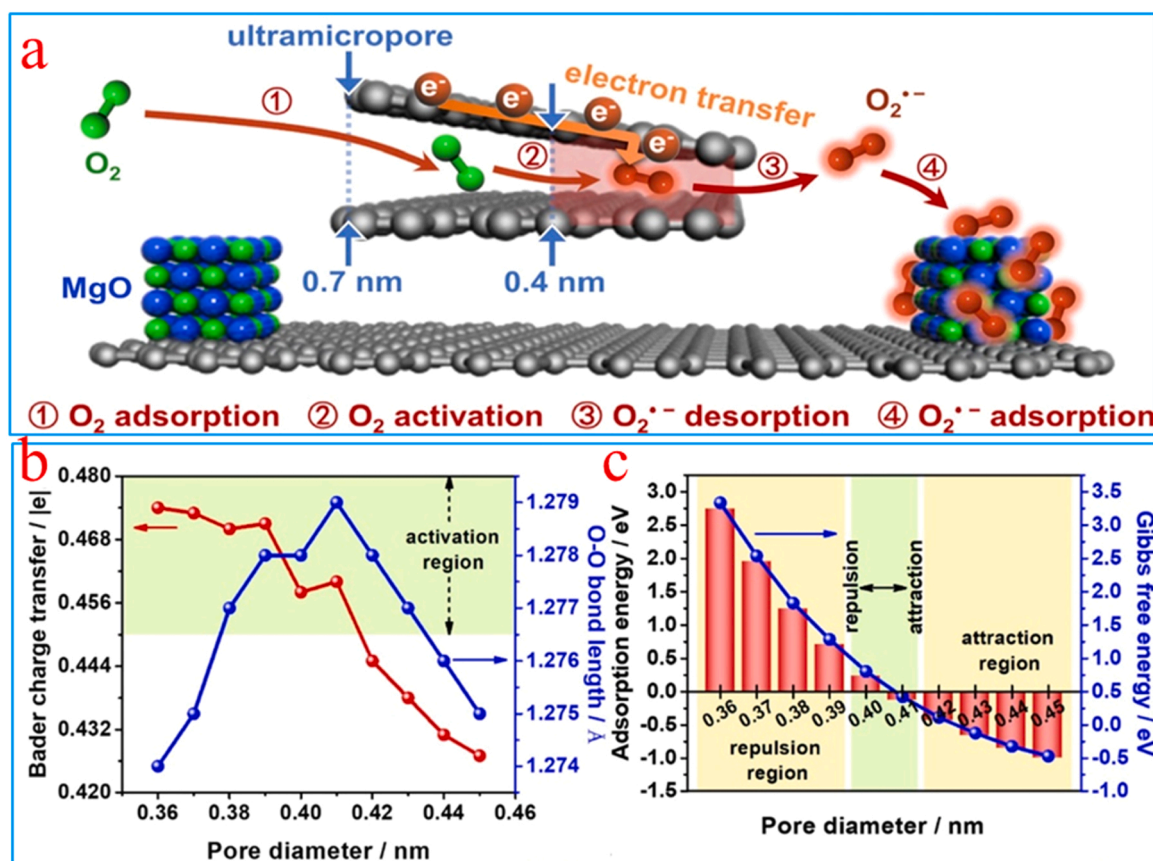


Fig. 2. (a) Proposed process of O_2 activation in the PC/MgO system, (b) Quantity of Bader charge transfer and corresponding O-O bond length of the confined O_2 molecule in the studied range of pore diameter from 0.36 to 0.45 nm, (c) Adsorption energy and corresponding Gibbs free energy of the confined O_2 molecule in the studied range of pore diameter from 0.36 to 0.45 nm.

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2.1.2. Copper species incorporated to carbons

Copper species are known as oxygen activating sites in biochemistry and in catalysis [53–56] and therefore copper-modified carbon materials were also used as media for the H_2S oxidative removal. Bandoz et al. [57] found that the performance of activated carbons mixed with bentonite binders containing copper species is higher than that mixed with binders containing iron or zinc species. This phenomenon highlighted the specific role of the copper species in oxygen activation. Support for this was in more elemental sulfur and SO_2 formed on the carbons with the Cu species than on that without them. The authors suggested that after mixing with the carbon phase, the copper species in

the binder migrate to the carbon phase and are fixed at the edges of graphene layers forming copper-peroxo complexes. Therefore, dicopper-dioxygen adducts were considered as the active sites for oxygen activation. The catalysts lost the ability to remove H_2S after all Cu^{2+} were reduced into Cu^{1+} and Cu_2S were deposited on the carbon surface.

Wang et al. [58] synthesized various valence Cu species-modified activated carbons and tested their H_2S removal performance in a moist and oxygen-containing atmosphere. They reported that Cu nanoparticles-modified activated carbon showed the highest H_2S removal capacity of 358.3 mg/g, followed by the Cu_2O - and CuO -modified activated carbons. Although the authors revealed that the

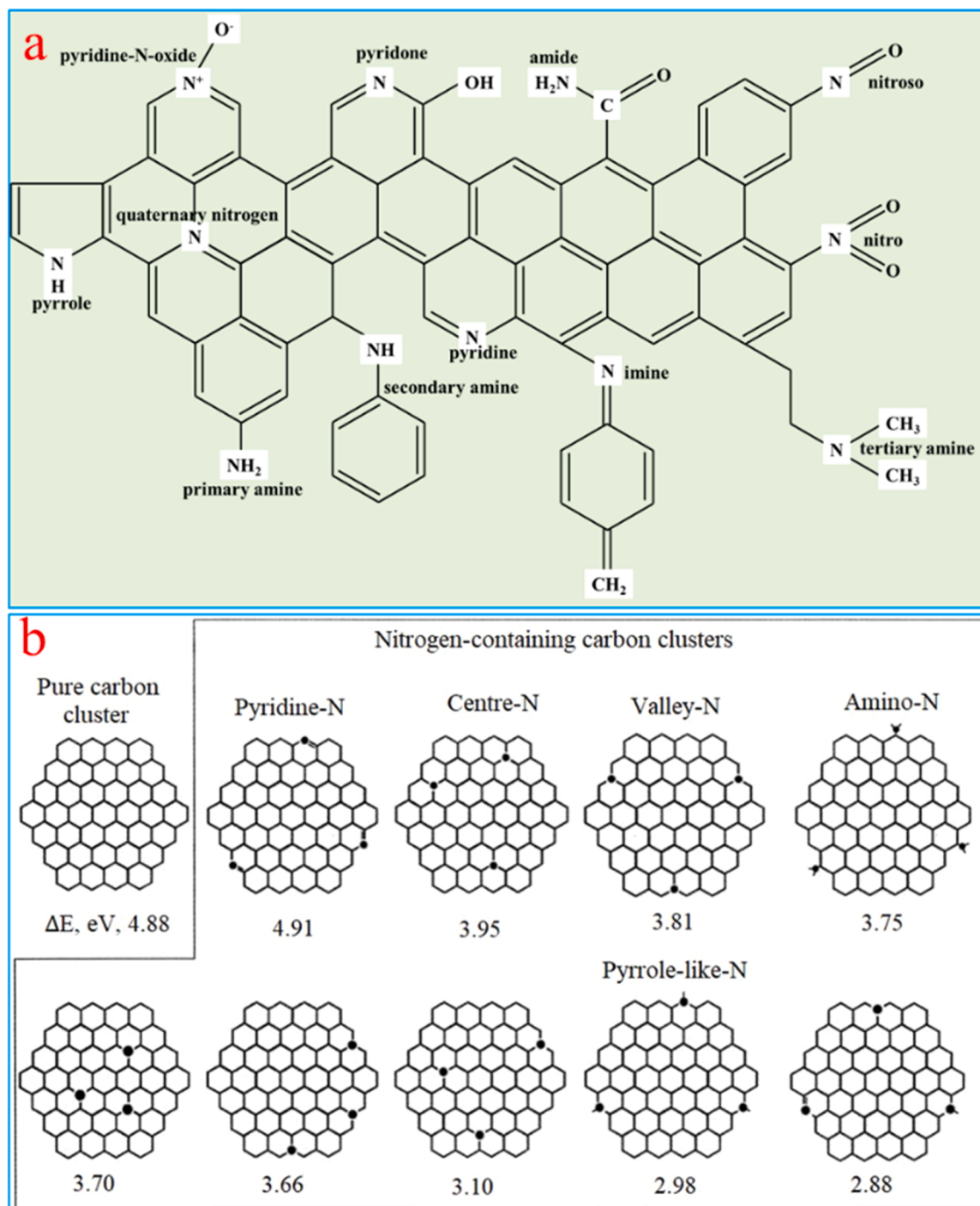


Fig. 3. (a) Types of nitrogen surface functional groups. (b) Structure and band gap values for model clusters of pure and nitrogen-containing carbons. (a) Reprinted with permission from Ref. [62] Copyright 2009, Elsevier (b) Reprinted with permission from Ref. [64] Copyright 2000, Elsevier.

desulfurization process included reactive adsorption and catalytic oxidation, and the later was considered as the predominant, they failed to provide more details on the catalytic oxidation process. In our opinion, their results might be a strong indication of the role of metallic copper species/nanoparticles in oxygen activation advancing H₂S catalytic oxidation. The stronger oxygen activation by the Cu nanoparticles might be related to their low reactivity towards H₂S at room temperature [59]. This hinders the rapid formation of CuS or/and Cu₂S, which have no ability to activate O₂. The above property of the Cu nanoparticles ensures a continuous release of Cu⁺ with the help of a weakly acidic environment that might be formed owing to the dissolution of H₂S in a water film. Then Cu⁺ activates O₂ through an alteration of its valence state [55]. In addition, the hetero-interface formed between the copper species and carbon phase might also contribute to oxygen activation through an alteration of an O₂ adsorption mode [60]. Owing to the significance of oxygen activation for H₂S oxidation, there is no doubt that the molecular or even atomic level insights on this process on copper species need to be studied in details.

2.1.3. Nitrogen atoms doped to carbon matrix

Nitrogen atoms doped into the carbon matrix can also act as sites for oxygen activation due to the modulation of the electronic structure of the carbon surface. As seen in Fig. 3a, the nitrogen species introduced to the carbon matrix exhibit various configurations, and they can be broadly classified into chemical N and structural N [61,62]. While the former refers to the N atoms in the form of surface functional groups, including amine (–NH₂), nitro (–NO₂) or nitroso (–NO) groups, the later corresponds to the N atoms inserted to the carbon skeleton, including pyridinic N (sp² hybridization), pyrrolic N (sp³ hybridization), and quaternary N (sp² hybridization) [63]. Only the latter are considered as doped, owing to their direct incorporation to the carbon rings.

Strelko et al. [64] suggested that the doped N atoms in a graphite lattice altered the band gap of a carbon matrix, changed an electron (charge) mobility and the electron work function at the carbon/gas interface, which remarkably affected the carbon performance as a catalyst in general. The authors calculated the band gap values of pure carbon and nitrogen-containing carbons with different configurations of these species. The results indicated that the carbons containing pyrrolic N have the lower band gap than that of pure carbon and the ones with pyridinic N (Fig. 3b). The lower band gap led to the higher charge mobility in the carbon matrix, thus efficiently promoting the formation of active oxygen species. Pan et al. [48] also indicated that the doped N atoms in the carbon matrix could enhance a π * electron migration in sp² carbon by conjugation, owing to the presence of localized unpaired electrons. This facilitated an electron transfer from the carbon matrix to the adsorbed O₂ molecules forming O₂•[−]. However, the authors did not illustrate which kinds of N configurations provide such an activity. In our opinion, the introduced N atoms alter the electronic structure of neighboring carbon atoms, which influences the adsorption of O₂ and the electron transfer from the carbon phase to O₂, thus making a contribution for oxygen activation [50,65].

2.2. Alkaline environment/basic pH

The enriched surface chemistry and electronic structure can not only participate in oxygen activation but it also can bring specific acid-base properties to the carbon matrix. H₂S is an acidic gas whose dissociation constants K_{a1} and K_{a2} are 9.6 * 10^{−8} and 13 * 10^{−14}, respectively. This causes that at certain conditions, provided by the carbon catalyst surface, H₂S exists rather as bisulfide and sulfide anions than as a neutral molecule. Therefore, understanding the influence of carbon surface pH on the catalytic oxidation mechanism of carbon-based catalysts is imperative.

Adib and Bandosz [66] indicated pH of the activated carbon surface as a very important descriptor of the catalyst's suitability for the H₂S removal from moist air streams. The authors found that moderately

acidic pH of carbon increased the contribution of sulfur species with S⁴⁺ and S⁶⁺ deposited on the surface as a result of H₂S oxidation (Fig. 4a). This is because in such conditions the dissociation of H₂S is inhibited and rather small amounts of HS[−] are formed, and converted on the surface to isolated S radicals, which are easy to be oxidized by oxygen. An opposite trend was found when the surface was basic. At such conditions a higher concentration of HS[−] led to hard-to-be-oxidized polymeric elemental sulfur as a predominant product. In later studies, Bandosz et al. [67,68] proposed an empirical and theoretical threshold in the carbon surface pH values, which could be considered as a cut-off for efficient H₂S catalytic oxidation on the carbon surface. To determine the theoretical value, they proposed the following steps of H₂S oxidation processes on carbon: (i) H₂S adsorption on the carbon surface, (ii) dissolution of H₂S in a water film, (iii) dissociation of H₂S in an adsorbed state in a water film, and (iv) a surface reaction with oxygen. They assumed that the equilibrium constants for H₂S adsorption, dissolution and dissociation are K_H, K_S and K_a, respectively. The surface reaction with oxygen was considered as a rate limiting step for the whole H₂S oxidation process. It was also presumed that the concentration of H₂S_{ads} was not higher than the solubility of pure H₂S in water. Based on the mentioned above, Bandosz et al. [67,68] proposed the following dependence of the HS[−]_{ads} equilibrium concentration:

$$\log(\text{HS}_{\text{ads}}^-) = \log(K_S) + \log(K_H) + \log(K_a) + \text{pH} + \log(\text{H}_2\text{S}_{\text{gas}}) \quad (1)$$

Therein log(K_a) = 7.2, K_S = 3.1; both values were calculated based on the solubility of pure H₂S at 25 °C in water (0.125 mol/L). K_H was obtained according to the ratio of H₂S_{ads} to H₂S_{ads-liq} owing to its dependence on the interactions of H₂S with carbon. K_H = 330 when the concentration of H₂S in the gas phase is 3000 ppm. Substitution of K_S, K_H, and K_a values in the above equation led to:

$$\log(\text{HS}_{\text{ads}}^-) = -4.2 + \text{pH} + \log(\text{H}_2\text{S}_{\text{gas}}) \quad (2)$$

The above equation revealed that, for carbons having average surface pH > 4.2, the concentration of HS[−] in the adsorbed state would be equal to H₂S in a gas phase (100% adsorption + dissociation). This value is lower than the first dissociation constant (pK_{a1}) of H₂S, indicating that the pH value only high enough for mild dissociation of H₂S is sufficient for its effective removal. Based on the proposed expressions, the authors calculated the ratio percentage of HS[−]_{ads}/H₂S_{gas}. They also normalized their experimental H₂S removal capacities (in mg of H₂S per unit pore volume of carbon) and analyzed their dependence on the surface pH values of carbons. The theoretical and empirical results are shown in Fig. 4b. As seen, although the threshold estimated from the experimental data (at around 4.5) is higher than the calculated one, both the calculated and experimental results showed the same trend expressed by a sharp increase in the adsorption capacity in the range of pH between 4 and 5. The discrepancy with the calculated value of pH might be caused by the fact that pH > 4.2 was obtained from the simplified expression without the exact value of the adsorption constant, K_H.

Based on the extensive studies of a large set of virgin carbons, Bandosz et al. [69], in their another study, proposed a plausible H₂S oxidation pathway depended on the carbon surface pH values. As seen in Fig. 4c, extremely acidic pH inhibited dissociation of H₂S on the carbon surface, limiting the H₂S removal capacity via catalytic oxidation. Moderate pH, estimated as larger than 4.5, in the pore system led to an enhancement in H₂S dissociation in a water film. While in such a condition elemental S, SO_x and H₂SO₄ were the mainly products, in a distinctively basic environment the high extent of H₂S dissociation ensured the formation of bulky sulfur polymers, resistant to oxidation, as the predominant product of surface reactions. The author considered that mechanism as valid, regardless the species governing the carbon surface pH values, and it was used in the explanation of the catalytic behavior in many followed-up works of different authors [52,70–72].

Interesting study of the effect of *in situ* local pH on the desulfurization performance was performed by Yan et al. [70], who studied the

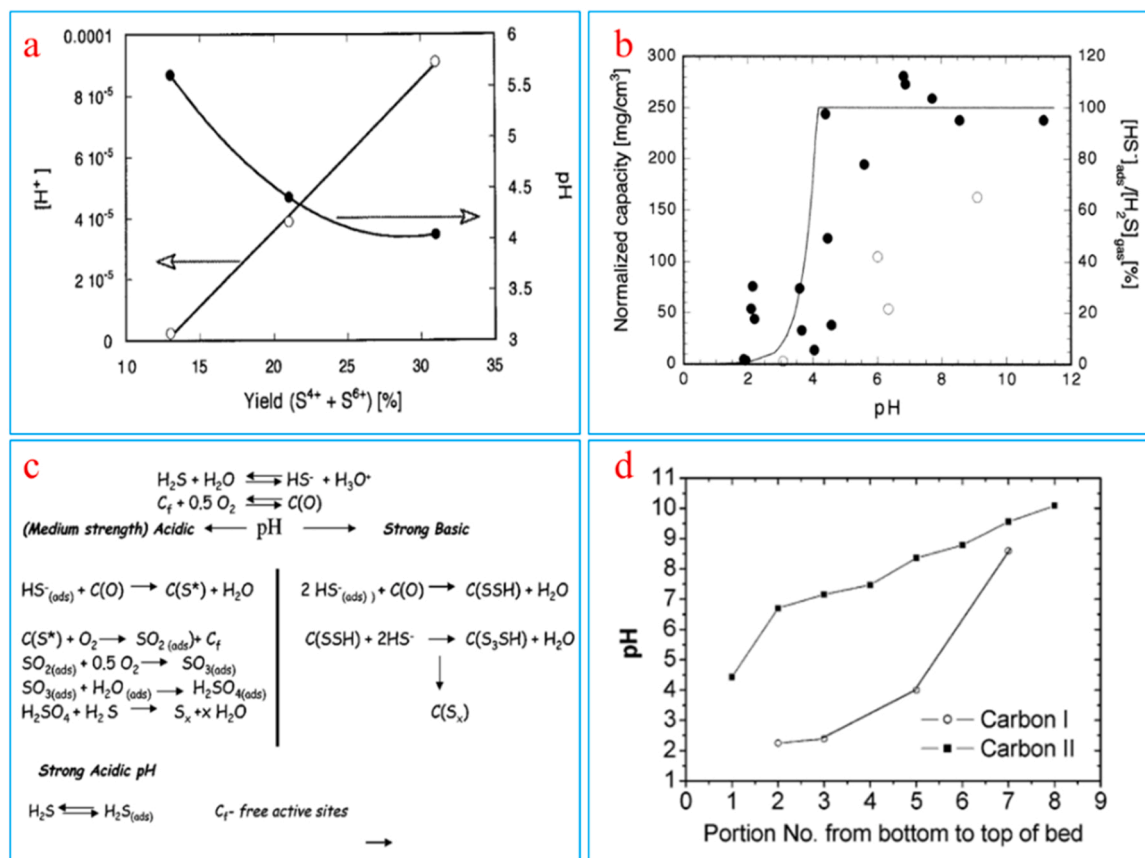


Fig. 4. (a) Yield of S^{4+} and S^{6+} versus pH of initial carbons and hydrogen ion concentration on the surface. (b) Normalized H_2S breakthrough capacity (in mg of H_2S per unit pore volume of carbon) versus pH of the carbon surface. (c) Proposed pathways of H_2S oxidation on unmodified activated carbons. (d) pH tendency of the exhausted activated carbons along the bed.

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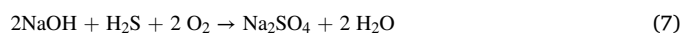
variation of local pH in the pore system, with the duration of desulfurization, on KOH-modified activated carbon. The trend in the pH values of activated carbon from each portion of an adsorption bed is shown in Fig. 4d. The pH values depended on the height of the bed. The authors suggested that both the dissolution of H_2S in the water film and the formation of sulfuric acids on the carbon resulted in a change of pH from basic to acidic in the portions of the bed first exposed to H_2S . The authors also considered that the variation in pH with the duration of desulfurization could remarkably influence the desulfurization mechanism. At the beginning of the adsorption process, since the surface pH of the original carbon was higher than pK_{a1} of H_2S , the concentrations of HS^- was high and the polysulfides could be formed. As the extent of the reaction progressed, surface pH gradually decreased from basic to acidic and thus the concentrations of HS^- ions decreased significantly. Thus, highly dispersed sulfur was formed and it was susceptible to be further oxidized into SO_2 and SO_3 . The further continuation of desulfurization resulted in a more acidic pH value and physical adsorption was a dominant process. This mechanism follows that proposed by Bandoz et al. [69].

As mentioned above, an alkaline environment on the carbon surface is needed for efficient H_2S dissociation, thus improving the H_2S catalytic oxidation performance. In order to increase surface basicity, researchers introduced various alkaline species onto the carbon surface, including caustics, basic salts, alkaline-earth metal oxides, and nitrogen-containing species addressed below.

2.2.1. Caustics and basic salts ($NaOH$, KOH , K_2CO_3 , Na_2CO_3)

Caustics and alkali metal salts exhibit strong basicity and solubility

in water, which makes them convenient media to adjust pH and thus to increase the extent of H_2S dissociation [73,74]. Bagreev et al. [75] found that the H_2S removal capacities on NaOH impregnated activated carbons depended on the content of NaOH on the surface. When 10 wt% of NaOH was loaded, the capacity increased 4–5 times compared to that on parent carbons. NaOH not only provided the basic environment but also reacted with H_2S by an acid-base neutralization reaction, leading to large amounts of HS^- formed. The enhancing role of NaOH in H_2S oxidation ceased after all of NaOH was consumed and formed sulfates. A similar result was obtained by Bashkova et al. [76], who also studied the selective catalytic oxidation of H_2S on NaOH modified activated carbons. Since KOH behaves similarly to NaOH, the above results are also suitable for KOH modified carbons [47]. The involved reactions on the NaOH-impregnated carbons were as follows [75]:

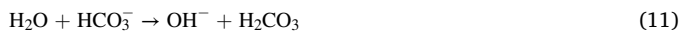


Tsai et al. [73] studied the H_2S removal performance on Na_2CO_3 or/and K_2CO_3 modified activated carbons. The authors found that these basic salts promoted dissociation of H_2S through the following mechanisms:



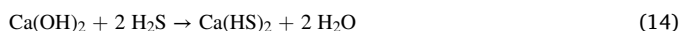


Here, we propose a different H_2S dissociation mechanism in moist conditions. Carbonate ions should be firstly hydrolyzed into bicarbonate ion/carbonic acid and hydroxyl ions in the water film. Then, the formed hydroxyl ions in dissociation of bicarbonate and carbonate resulted in dissociation of H_2S .

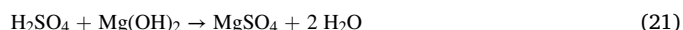
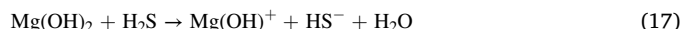


2.2.2. Alkaline-earth metal oxides-modified carbons (MgO, CaO)

Since MgO and CaO are medium strength bases, their low reactivity towards H_2S at room temperature and low solubility in water allowed continuous H_2S dissociation during desulfurization process on Midas® catalytic carbon, on which 60 wt% of sulfur was deposited on the surface in the air desulfurization process [47]. Bagreev et al. [47] proposed the following H_2S oxidation mechanisms on these catalysts:



Similar results were also obtained by Yang et al. [77], who studied the H_2S removal on MgO-impregnated activated carbon and found that the desulfurization products included elemental S and sulfates. Based on the above, the authors supplemented the reactions involved in the desulfurization process:



2.2.3. Nitrogen surface groups

Besides the mentioned above ability of nitrogen species to activate oxygen, they are also known as increasing the surface basicity and polarity of a carbon phase [63,78], thus significantly affecting its catalytic oxidation performance towards H_2S [50,79–86]. In the studies of the Bandosz's group [10,87–89], it was suggested that the enhanced H_2S removal capacities of carbon catalysts after the nitrogen modification

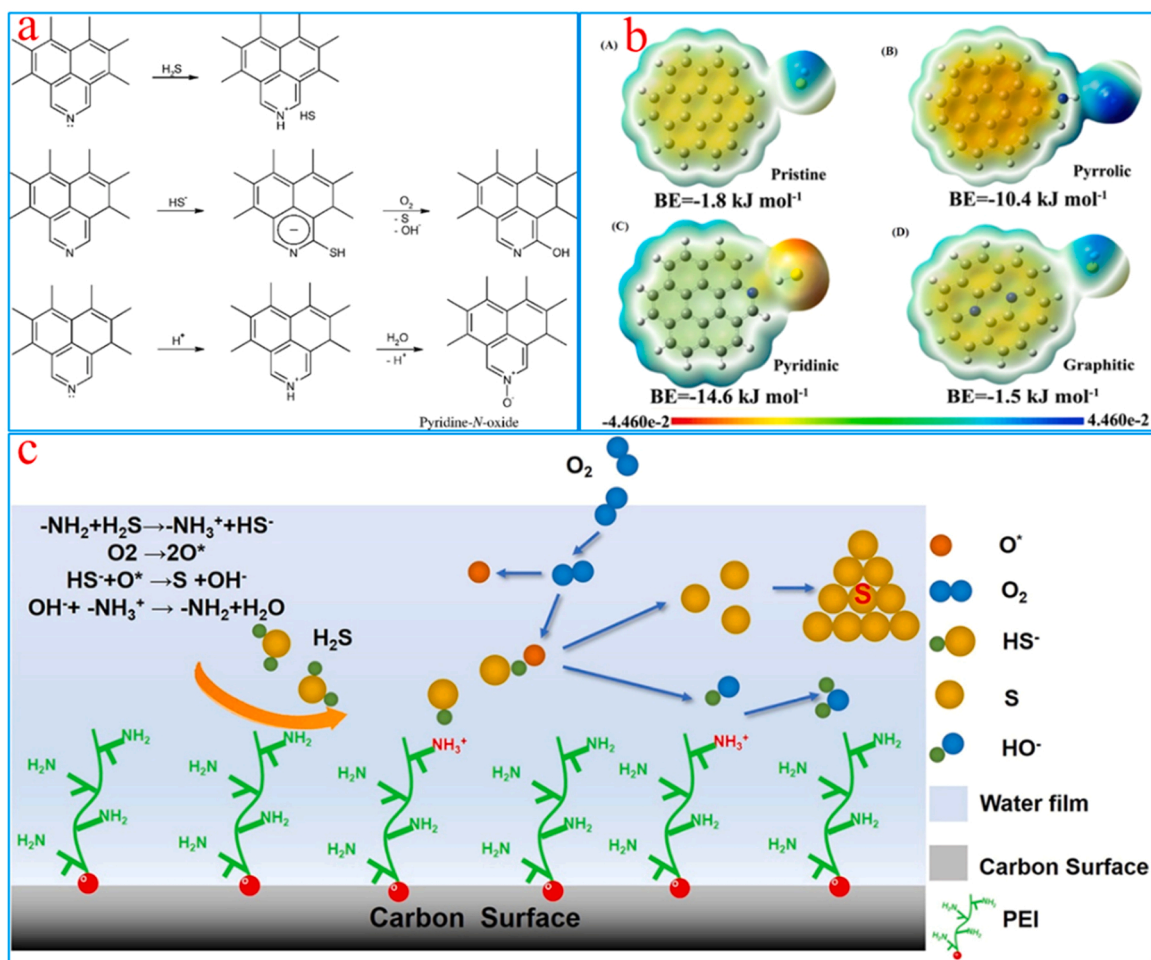


Fig. 5. (a) Possible surface reaction paths. The condensed aromatic rings represent the fragments of graphene layers. (b) The atomic geometry of H_2S molecule binding on (A) pristine carbon surface, and carbon surface doped with (B) pyrrolic N, (C) pyridinic N and (D) graphitic N. The grey, yellow, blue and white spheres are C, S, N and H atoms, respectively. (c) Catalytic mechanism of the H_2S oxidation process over MCNs-PEI-25 using amine group of $-\text{NH}_2$ as representation. (a) Copyright 2007, American Chemical Society. [92] (b) Copyright 2015, Elsevier [90]. (c) Copyright 2021, Elsevier [93].

resulted from quaternary and pyridinic nitrogen configurations, which acted as basic sites during desulfurization promoting dissociation of H_2S . Therefore, that activity might double-up with that mentioned above in the oxygen activation. Similar results were also found by Yu et al. [90] and Sun et al. [91]. The former reported an approximate linear relationship between the H_2S removal capacity and the N content for carbons of similar porosities [90], and the latter quantified the relationship between the H_2S removal capacity and the pyridinic N content by an indication of a linear dependence between these two measures [91].

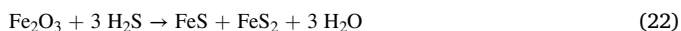
In another study of Bandoz et al. [92], the authors proposed an oxidation mechanism of H_2S on pyridinic N-modified carbon materials. As shown in Fig. 5a, the pyridinic N attracted H_2S resulting in its dissociation into HS^- ; the dissociated HS^- was then chemisorbed on the carbon adjacent to pyridinic N to form a stable compound. This species was then oxidized by O_2 forming elemental sulfur, and the pyridinic compound converted to a pyridone. In order to better understand the role of pyridinic N in H_2S catalytic oxidation, Yu et al. [90] calculated the binding energies of H_2S with various N configurations. As seen in Fig. 5b, the binding energy of H_2S with pyridinic N is much higher than that with other N configurations, indicating the pyridinic N as the primarily sites for H_2S dissociation.

Wang et al. [93] studied the H_2S removal on polyethyleneimine (PEI) modified mesoporous carbon nanosheets. The authors found that the amine groups of PEI promoted the dissociation of H_2S . As seen in Figure 5c, H_2S reacted with $-\text{NH}_2$ group in PEI to form HS^- and $-\text{NH}_3^+$, then the HS^- further reacted with the active oxygen species (O^*) to generate elemental S and OH^- . After that, the formed OH^- reacted with $-\text{NH}_3^+$ to form $-\text{NH}_2$ group and H_2O . Similar result was also found by Sun et al. [94], who investigated the H_2S removal performance on amino-functionalized lotus root-like carbon nanofibers.

2.3. Redox activity of Fe-containing species

Featuring of various oxidation state active in redox reaction, Fe-containing species, especially Fe_2O_3 , were widely used as catalysts for H_2S catalytic oxidation at mid-temperatures [34,95–98]. However, their catalytic activities dramatically weakened at room temperature owing to the formation of stable Fe-S bonds [99]. Therefore, the combination of Fe-containing species with carbon materials is considered as an effective strategy for improving the H_2S catalytic removal, due to the involvement of a synergistic effect [100].

Bagreev et al. [47] studied the H_2S removal from moist air on a carbonaceous material containing the Fe_2O_3 species. They found that the H_2S breakthrough capacities on modified carbons were much higher than on the sample without Fe_2O_3 . The experimental results indicated that elemental S was a dominant product, and the activity of Fe_2O_3 followed the reactions in which the catalyst was regenerated:



In that study, the authors also highlighted the importance of conjunction of Fe_2O_3 with the carbon phase, however an in-depth discussion on it was missing. In our opinion, this conjunction might contribute to desulfurization by promoting re-oxidation of Fe-S bonds into elemental S and Fe_2O_3 by the active oxygen species, which might be generated on the carbon materials via oxygen activation discussed above [101,102].

Besides Fe_2O_3 , iron (hydr)oxides were also used as an active phase for enhancing the gas desulfurization performance of the carbon-based catalysts. Arcibar-Orozco et al. [103] investigated the H_2S removal from moist air on the composites of graphite oxide (GO) with either magnetite or two-line ferrihydrite. The performance of the as-prepared composites depended on the nature of iron (hydro)oxide and the

added amount of GO. The combination of magnetite with GO increased the amount of OH reactive groups and surface heterogeneity, thus increasing the H_2S removal. Whereas an opposite result was found on the composites of ferrihydrite with GO. The addition of the latter reduced the amount of OH groups in ferrihydrite and also promoted the formation of sulfates during desulfurization. The authors indicated elemental sulfur and ferric and ferrous sulfates as the dominant reaction products, and they proposed a redox reactive mechanism on the received composites. As seen in Figure 6, H_2S molecules or/and the dissociated HS^- reacted with the OH groups of ferrihydrite/magnetite (Fig. 6I) to form iron (III) sulfides (Figure 6II). This process was enhanced by adsorbed water that promoted both, the dissolution/dissociation of H_2S and the surface hydroxylation of the iron phase. Oxidation of sulfide into elemental sulfur in the following step occurred in an oxygen atmosphere and the latter species deposited on the surface of the composites (Figure 6III). The formation of ferric and ferrous sulfate during desulfurization was attributed to the reaction between H_2S and the surface Fe(III) (Figure 6IV), where the reduction of Fe (III) to Fe(II) by HS^- led to the formation of SO_2 (Fig. 6V), that was then transformed into SO_3 in an oxidizing atmosphere and formed SO_4^{2-} with the assistance of adsorbed water (Figure 6VI). This process also led to the formation of szomolnokite (Figure 6VII), which eventually transformed into ferric sulfate (Figure 6VIII) with the help of atmospheric O_2 .

3. Factors influencing H_2S catalytic oxidation: Insight into the mechanism of the processes

3.1. Moisture in feed gas

Carbon surface is hydrophobic in its nature owing to its high degree of aromatization or/and the presence of graphene-like sheets. However, oxygen containing groups on the surface increase the ability of carbon to adsorb water. Many studies have established that the adsorbed water has a very important role in the H_2S removal at room temperature. It is because a thin water film formed in micropores, and even in mesopores of carbon materials, dissolves H_2S and promotes its dissociation. Klein et al. [104] indicated that the formation of the water film on the internal surface of carbon is essential for catalytic oxidation of H_2S at low temperature. The authors also proposed an oxidation mechanism of H_2S on the carbon surface in the presence of water. As shown in Fig. 7a, the H_2S and O_2 molecules upon diffusion into pores were firstly dissolved in the water film, where the H_2S molecule dissociated into HS^- . The O_2 molecule was adsorbed on the carbon surface and upon being activated into reactive O^* species, it oxidized dissociated HS^- into elemental S.

Yuan et al. [105,106] found that the formed water film could also mechanically and continuously clean the active sites and this process kept the latter free and accessible for the reactants, thus slowing down deactivation of the catalysts. Although this is a very interesting finding, the authors did not give any mechanistic details on how the water film could achieve this goal. It is possible that this phenomenon might relate to the continuous refreshment of the water film owing to the flow of moist feed gas.

Bandoz et al. [68,69,109] reported that activated carbons after pre-humidification showed a much higher H_2S removal efficiency than their dried counterparts. Moreover, they found a threshold in the amount of adsorbed water, as shown in Fig. 7b. The results suggested that the amount of preadsorbed water should not be greater than 3 mmol/g carbon. Beyond this value, a decrease in the capacity was observed owing to the filling of small pores by water, which limited a direct contact of HS^- with the carbon surface in these pores [68,69].

The moisture content in feed gas, indicated as its relative humidity (RH), also strongly influences the H_2S removal [106,110,111]. Subrenat et al. [110] found that the H_2S removal capacity firstly increased and then decreased with increasing RH, and optimal RH was $\sim 60\%$. The enhanced performance after the introduction of moisture was linked to

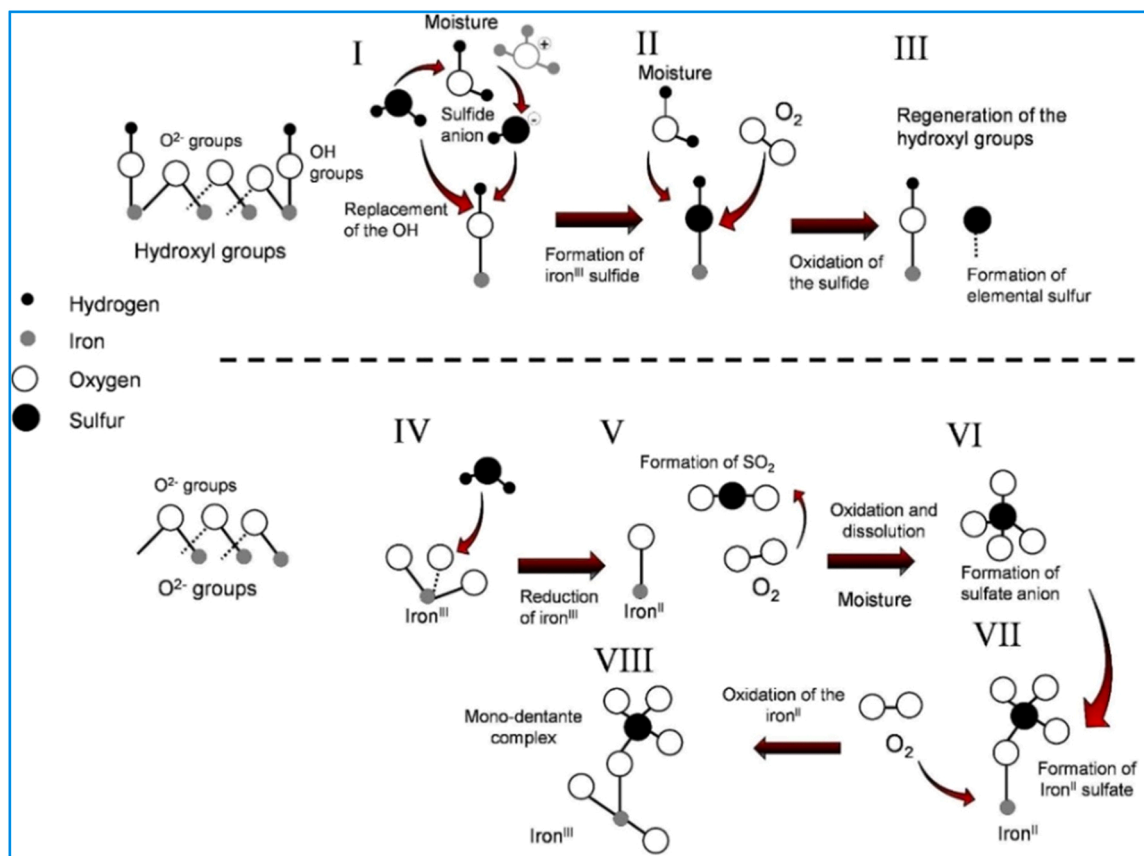


Fig. 6. Reactive adsorption mechanism of H_2S on the surface of the composites studied. Copyright 2015, American Chemical Society. Reprinted with permission from Ref. [103].

the formation of the water film, which promoted dissociation of H_2S and O_2 , and this is consistent with the results obtained by Klein et al. [104]. Excess water might fill the micropores of catalysts hindering the accessibility of reactants, decreasing the performance, as discussed above.

Trovarelli et al. [107] explored the effect of RH on an H_2S oxidation rate on the carbon surface (Fig. 7c), and their results showed some similarity to those of Subrenat et al. [110]. The H_2S oxidation rate dependence on RH showed a volcanic curve. While optimal RH was at around 20%, the lowest performance was in the absence of water. Three different regions were identified in the curves. Region I was at low RH, where the oxidation rate increased with an increase in RH. This increase was a result of the catalytic effect of water deposited in the pores in accelerating the oxidation reaction. In Region II, a decrease in the H_2S oxidation rate was observed, which might have been caused by the filling of micropores. In Region III, the constant oxidation rate was observed, which indicated that the reaction at this stage was probably running inside large pores or on the outer surface of particles.

H_2S oxidation kinetics on the carbon surface at different RH were also studied by Bouzaza et al. [108]. The authors considered that the oxidation process followed the Langmuir–Hinshelwood reaction rate model. The initial reaction rate was expressed as:

$$r_i = k \cdot (K \cdot C_0) / (1 + K \cdot C_0) \quad (25)$$

where r_i is the reaction rate ($\text{mg} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$); k is the L–H rate constant ($\text{mg} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$); K is the Langmuir adsorption constant ($\text{m}^3 \cdot \text{mg}^{-1}$).

From Eq. (25), the values of k and K for the catalyst at different RH were calculated, and the results were shown in Table 1. The increased k values with increasing RH revealed a positive role of water in H_2S catalytic oxidation. A small effect of RH on the adsorption constant K might indicate that the competitive adsorption of moisture in feed gas with

that of H_2S on the carbon surface is counterbalanced by an increase in dissolving O_2 and H_2S in the water film.

Huang et al. [112] in their study of $\text{Cu}(\text{OH})_2$ -impregnated activated carbons as the H_2S removal media analyzed the role of water. Consistently with the results of Bandoz et al. [109], the authors found that pre-humidification had a positive effect on the H_2S removal, owing to the formation of the water film on the carbon surface. An opposite effect of water was found when the catalysts were directly exposed to H_2S in moist conditions. In that case the breakthrough times remarkably decreased with increasing RH from 0% to 80%. The negative role of water was mainly attributed to competitive adsorption between H_2O and H_2S , and to the contribution of water to the reduction of copper (II) to copper (I) species during desulfurization, resulting in surface deactivation.

Water in challenge gas was also found as having a negative effect on the hydrogen sulfide removal from digester gas on catalytic carbons enriched with a basic/alkaline phase [113]. Even though water is known to promote H_2S dissociation [69], in the case of digester gas it reacted with CO_2 forming carbonic acid and also contributed to the formation of sulfurous acid, which deactivated the basic catalytic sites, resulting in the marked decrease in the H_2S removal capacity.

3.2. Heterogeneity of pore sizes/pore volume

A large surface area, high pore volume, and hydrophobic surface are unique assets of carbons and they distinguish them from other catalysts. While the development of the surface area helps in exposing a large number of active sites participating in H_2S catalytic oxidation, the expanded pore volume provides space for the storage of the desulfurization products. In addition, connected pore channels in all directions allow diffusion of H_2S and increase the accessibility of active sites.

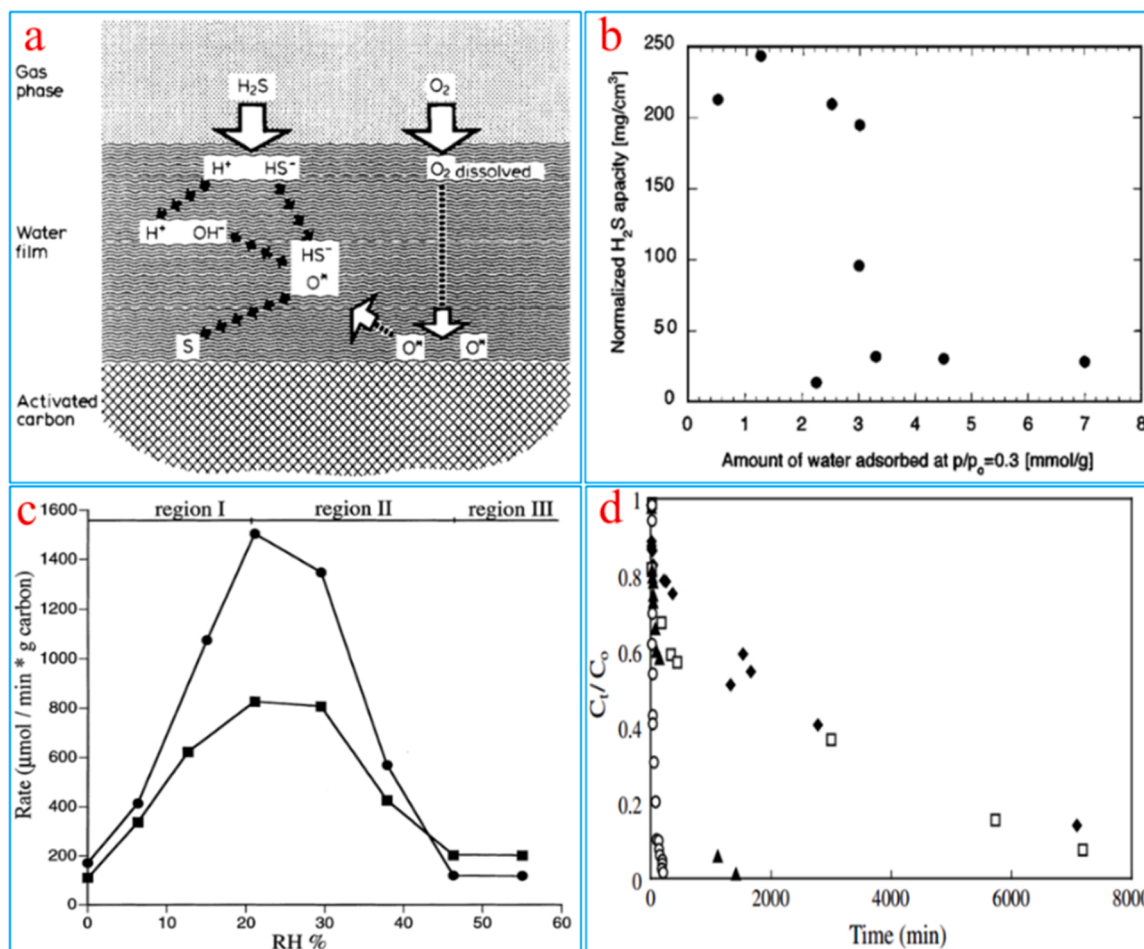


Fig. 7. (a) Mechanism of H₂S oxidation on activated carbon. (b) Normalized capacity versus amount of water adsorbed at $p/p_0 = 0.3$ and 293 K. (c) Rate of hydrogen sulfide oxidation at different RH: (■) $T = 298$ K, (●) $T = 313$ K. (d) Effect of the RH on the kinetic oxidation for Actitex RS1301: (◆) 0 % RH; (□) 20 % RH; (▲) 50 % RH; (○) 100 % RH.

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Table 1

Values of the L-H model constants for Actitex RS1301 fibers under air atmosphere [108].

Parameter	K ($\text{m}^3 \cdot \text{mg}^{-1}$) $\cdot 10^4$	k ($\text{mg} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$)
Actitex RS1301, RH = 0 %		0.2 ± 0.02
Actitex RS1301, RH = 20 %	6 ± 1	0.7 ± 0.06
Actitex RS1301, RH = 40 %	5 ± 0.8	1.7 ± 0.1
Actitex RS1301, RH = 50 %		1.3 ± 0.1
Actitex RS1301, RH = 100 %		2 ± 0.2

According to International Union of Pure and Applied Chemistry (IUPAC), the pores in the carbon materials are classified into ultramicropores (<0.7 nm), micropores (0.7–2 nm), mesopores (2–50 nm) and macropores (> 50 nm), and they play different roles in the H₂S catalytic oxidation.

Bandosz et al. [114] studied the effect of the pore structure and surface area of activated carbons on the H₂S removal. Three virgin activated carbon (WVA-1100, Maxsorb® and Xtrusorb®, designated as W, M, C, respectively) were selected. The highest surface area and micropore volume were found in M and the lowest- in C. Both, the total pore volume and mesopore volume decreased in the order of $W > M > C$. The authors found that the H₂S removal process on C and M mainly relied on physical adsorption of H₂S, and their structural parameters were almost preserved after desulfurization. Both physical adsorption and catalytic oxidation of H₂S occurred on W, and this carbon presented

the highest H₂S removal capacity of 47 mg/g. The experimental results suggested that there is no direct relationship between the performance of carbons and the surface area. Moreover, small pores in activated carbons favored the physical adsorption of H₂S due to their high adsorption potential, and mesopores favored the formation of the water film that promoted the catalytic oxidation of H₂S.

In their following study, Bandosz et al. [69] found that the heat of H₂S adsorption (Q_{st}) directly depended on a relative microporosity expressed as a ratio of the volume of micropores to the total pore volume, with $R^2 = 0.93$. This indicated the critical role of micropores in H₂S adsorption that is the first step for its catalytic oxidation on the carbon surface. The micropores are high energy centers attracting the small H₂S molecules at ambient conditions. The authors suggested that the speciation of the products of catalytic oxidation depend on the pore sizes. In the case of very microporous carbon, sulfuric acid was the predominant oxidation product. It was because the sizes of pores prevented the formation of bulky sulfur polymers and isolated sulfur radicals existing there were easily oxidized to SO₂ and then H₂SO₄ was formed. In pores with sizes enabling the formation of polysulfides, oxidation was limited and elemental sulfur was the predominant product of surface reactions.

In another study from the Bandosz's group [115], three activated carbons manufactured by Westvaco (wood based, H₃PO₄ activated), namely BAX-1500, WVA-900 and WVA-1100, were used to study the effects of the porous structure on the desulfurization performance. The experimental results indicated that the H₂S removal capacities of three

carbons decreased in the same order as their surface areas and volumes of micropores. Nonetheless, R^2 for the dependences of the catalytic performance on the surface area and pore volume were only 0.66 and 0.68, respectively, which indicated a very weak correlation and a possible influence of other factors. Additionally, the H_2S removal capacities of carbons were negatively related to the volumes of pores smaller than 0.5 nm, which suggested that they might not participate in the direct H_2S removal. The factor which might influence the latter, and which has not been discussed in that work is the hydrophobic nature of these pores and the absence of water molecules. The authors also found a good correlation between the H_2S removal capacity and the volumes of pores larger than 1 nm. The results suggested that the H_2S removal process occurs in pores which are either large enough for functional groups to exist or small enough for a water film to be formed at a relatively low humidity level.

The roles of small pores as oxygen reservoirs was indicated by Seredych and Bandoz by analyzing the H_2S removal from digester gas on commercial catalytic carbons [113]. Even though oxygen was not supplied in challenge gas, elemental sulfur was detected on the surface of the exhausted catalysts and its presence was linked to the effect of oxygen likely adsorbed in very small pores owing to the strong adsorption potential there.

The role of the pore structure in H_2S oxidation at ambient temperature was also studied by Ling et al. [52]. They used two series of Na_2CO_3 -impregnated activated carbon fibers (ACFs) as the H_2S removal media. The authors found a linear relationship of the saturation sulfur capacity on the pore volumes, with a correlation coefficient (R^2) of 0.96. For the volumes of pores with sizes larger than 0.7 nm, the correlation coefficient was $R^2 = 0.997$. This trend was explained by the preferential deposition of sodium carbonate species in pores with sizes > 0.7 nm, which resulted in a high concentration of HS^- in their water film (Fig. 8a). The authors also found that the surface distribution of H_2S

oxidation products was affected by pore sizes of the catalysts; in pores with sizes > 0.7 nm elemental sulfur was the main products, whereas H_2SO_4 was mainly deposited in smaller pores. Although this finding is similar to the results obtained by Bandoz et al. [69], a different explanation was provided. Ling et al. [52] suggested that the formation of elemental S in pores with sizes > 0.7 nm was the result of a low density of dissociatively adsorbed oxygen in these pores, while a higher density of dissociatively adsorbed oxygen in smaller pores resulted in the formation of H_2SO_4 . Even though oxygen has a tendency to adsorb in small hydrophobic pores, and the effect of ultramicropores on the formation of active oxygen species was demonstrated by Pan et al. [48], the absence of the results reporting the density of dissociatively adsorbed oxygen in these pores makes this explanation somehow speculative. Anyway, this explanation does not make invalid that one proposed by Bandoz et al. [69], since active oxygen existing in small pores could advance oxidation of sulfur radicals formed there.

Besides the porosity influencing the H_2S removal activity, the pore structure also affected the oxidation of H_2S to SO_2 . Schwartz et al. [117] found that during desulfurization, the micropores with sizes below 1 nm made a great contribution to the formation of SO_2 , and the latter was effectively trapped by the pores with width of 0.7 nm, owing to their closest size to that of SO_2 molecule, whose size, mentioned in that study, is about 0.6 nm. This finding addresses the activity of the small pores in sulfur oxidation from another angle than those presented by Bandoz et al. [69] and Ling et al. [52]. Schwartz et al. [117] also reported that on mesoporous carbons there was a delay in an SO_2 breakthrough time compared to the carbons having a high contribution of micropores smaller than 1 nm. That delay was linked to more SO_2 dissolved in the water film, which led to the formation of H_2SO_4 or sulfates.

The roles of micropores and mesopores in the H_2S catalytic removal were also studied in detail by Long et al. [116], who prepared a series of Na_2CO_3 modified carbon aerogels containing inter-particle mesopores

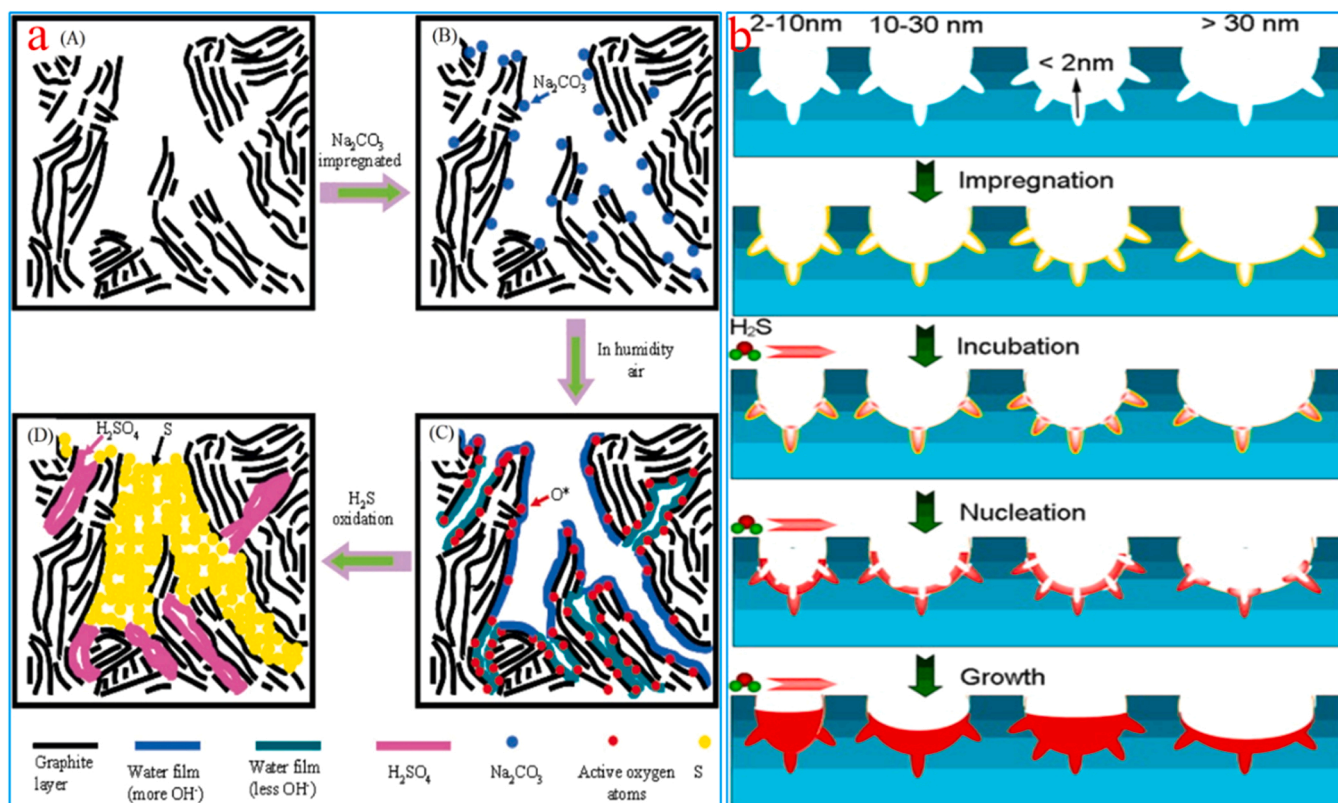


Fig. 8. (a) Schematic representation of H_2S oxidation and sulfur species deposition in the pores: (A) original ACFs; (B) impregnated ACFs; and (C, D) ACFs before and after desulfurization, respectively. (b) Schematic representation of sulfur dispositions on carbon aerogels with different microstructures.

(a) Copyright 2010, American Chemical Society [52] (b) Copyright 2011, Elsevier [116]

and intra-particle micropores. As seen in Fig. 8b, the Na_2CO_3 species preferred to deposit in micropores and remarkably increased pH of the water film. This led to an increase in the extent of H_2S dissociation. The authors suggested that in these micropores there were some active sites that promoted oxidation of the dissociated HS^- by the dissociatively adsorbed oxygen/ active oxygen species into elemental S and SO_x , however, the specific active sites were not identified in that study. In the light of the mechanism of oxygen activation on carbons discussed above, these sites might be associated to the defects in the carbon matrix [50]. The formed atomic S could self-organize into a S_8 cluster with sizes of 0.69 nm [118], which, when suspended in the water film, readily diffused along the carbon surface from the intra-particle micropores to the inter-particle mesopores. After that, these S_8 clusters nucleated spontaneously and coalesced into large size sulfur agglomerates on the surface of mesopores with the duration of desulfurization. This finding/hypothesis is very important but it is not clear which physical forces governed the diffusion of S_8 clusters in the water film.

Regarding the diffusion of sulfur into small pores, that mechanism was addressed in the early studies of Bagreev and Bandoz [47], when they analyzed the exceptional performance of Midas® catalytic carbon. That carbon contained ~30% of CaO/MgO finely dispersed within a microporous carbon matrix. Since after the H_2S catalytic conversion almost all pores were filled with elemental sulfur, the authors concluded that sulfur formed on the catalytic centers of the basic nature migrated to small pores of carbon in the vicinity of those centers, resulting in a gradual filling of pores and release of catalytic centers for further H_2S molecules. That migration was governed by the affinity of sulfur to a hydrophobic surface and by a strong adsorption potential in small pores.

The carbon aerogels reported by Long et al. [116] exhibited a H_2S removal capacity of 2260 mg/g. The excellent performance was attributed to their unique intra-particle micropore and inter-particle mesopore structures, where the micropores acted as the reactors for H_2S oxidation and the mesopores provided the space for the storage of the products. In our opinion, the excellent performance might also relate to

the operation conditions, such as the desulfurization atmosphere and the ratio of O_2 to H_2S . In this study, the authors highlighted the great importance of the sizes of mesopores for the H_2S removal performance. They suggested that in the mesopores of small sizes, sulfur clusters could easily coalesce with each other into large agglomerates, which allowed their epitaxially growth and limited the coverage of the active sites. The situation was reversed in the mesopores with large sizes, where the sulfur clusters were readily isolated and hardly coalesced, and thus their growth progressed directed along the carbon surface. In this case the active sites were easily covered and their catalytic performance greatly decreased. However, the definite cut-off size of the mesopores for the sulfur cluster coalescence were not given by the authors.

Based on many efforts linking different sizes of pores to the catalytic oxidation of H_2S , a consensus can be found that the ultramicropores promoted further oxidation of elemental sulfur resulting in the formation of sulfuric acid with the help of water. In micropores bulky sulfur polymer resistant to oxidation could be formed, while the mesopores and macropores provided enough space for the storage of the oxidation products, mainly elemental sulfur and sulfates.

3.3. Oxygen groups incorporated to the carbon surface

Owing to the unique electronic and hybrid structure of carbon materials, oxygen-containing functional groups are inevitably present on their surfaces, and they significantly influence carbon surface pH and provide some level of hydrophilicity to the otherwise hydrophobic surface. Fig. 9a shows various possible configurations of the oxygen-containing functional groups on the carbon surface [119], mainly pyrones, carboxylic acids, carbonyls, lactones and carboxylic anhydrides. Different groups bring different properties, and of course, they are expected to affect the H_2S catalytic oxidation process.

According to their dissociation constants, the oxygen containing groups on the carbon surface can be classified into acidic and basic ones. While the former includes carboxylic acids, lactones, carboxylic

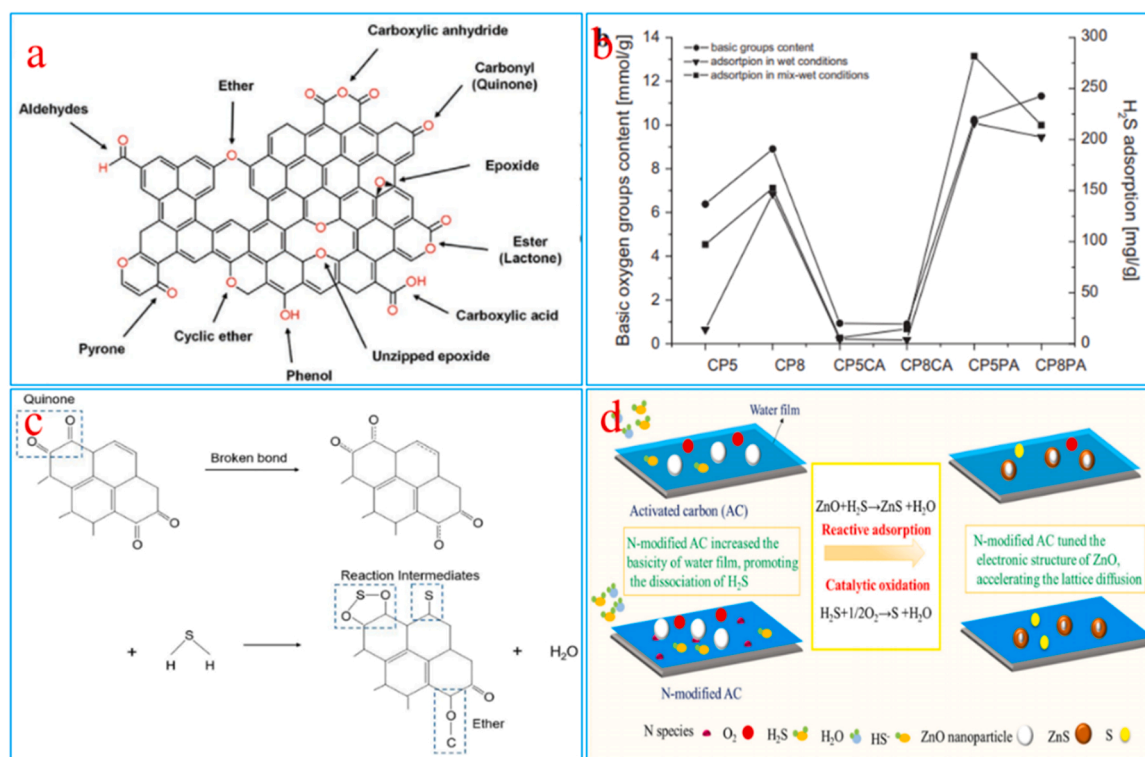


Fig. 9. (a) Possible O-configurations in carbon. (b) Dependence of H_2S sorption capacity on basic surface groups content. (c) Changes of the functional groups on AC during H_2S oxidation. (d) The proposed H_2S removal mechanism on ZnO supported N modified activated carbon adsorbents.

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anhydrides, phenols and carbonyl groups, the latter are pyrones and benzoquinone groups [123]. Numerous studies reported that the acidic oxygen groups on the carbon surface inhibit the dissociation of H_2S and are unfavorable for the H_2S removal, and an opposed trend was found for the basic oxygen groups [66,69,124]. Pietrzak et al. [120] found that there is a clear correlation between the content of the basic oxygen groups on the carbon surface and the H_2S removal efficiency, as shown in Fig. 9b. Similar results were reported by Feng et al. [125], who suggested that the basic oxygen groups were the active sites for the H_2S retention through acid/base interactions. In addition, the basic oxygen groups, such as pyrones and benzoquinones, can be also the active centers for H_2S catalytic oxidation owing to their excellent ability to transfer electrons from the carbon matrix to adsorbed oxygen [126,127].

The oxygen-containing functional groups were also found to be capable to react with H_2S , or/and oxidize it. Zhu et al. [121] reported that reactions of H_2S with quinones and carbonyl groups resulted in breaking $\text{C}=\text{O}$ and $\text{C}=\text{C}$ bonds, leading to the formation of intermediates with $\text{S}-\text{O}$ and $\text{C}-\text{S}$ bonds (Fig. 9 C). The latter bonds tended to form elemental sulfur while the $\text{S}-\text{O}$ bonds likely led to SO_2 in an O_2 enriched atmosphere. Interestingly, the authors also found that the $\text{S}-\text{O}$ bonds formed sulfate when there was a sufficient quantity of the oxygen-containing functional groups on the surface. Zhu et al. [121] also suggested that the oxygen-containing functional groups participated in oxidation of SO_2 into sulfates, however, they did not illustrate which kinds of groups could follow this path. Another pathway, not discussed by Zhu et al., is a role of oxygen groups in promoting an electron transfer from the carbon matrix to O_2 leading to its activation [128,129], and thus to deep oxidation of the $\text{S}-\text{O}$ bonds to form sulfates.

Yang et al. [122] and Chen et al. [130] studied H_2S catalytic oxidation on a ZnO/N -modified activated carbon composite in an oxygen free-atmosphere. The experimental results indicated that besides ZnS , the surface reaction products also included elemental S . Similar results were also reported in another work of Yang et al. [77], where the authors additionally introduced MgO into ZnO -modified activated carbon, and the sulfur-containing products contained ZnS , elemental S and sulfates. Since both studies were performed in anaerobic conditions, and ZnO has no ability to oxidize H_2S , the authors suggested that the oxygen sources needed for H_2S oxidation originated from the oxygen containing species on the activated carbon surface. Interestingly, it was found that activated carbon itself, in spite the presence of the oxygen groups on its surface, did not contribute markedly to the H_2S removal. These findings indicated that the oxygen-containing groups on the carbon surface need to be activated to play a role in H_2S oxidation. Unfortunately, the authors did not elaborate the activation mechanism in their studies. It is possible that a basic environment due to MgO or/and nitrogen-containing species promotes this process.

3.4. Composition of challenge gas/oxygen content in challenge gas: atmosphere effect

During the practical application of the gas desulfurization process, one needs to keep in mind that in challenge gas H_2S only accounts for a small amount, at a ppm level, and dominant molecules are CO , CO_2 , H_2 and CH_4 . These gases have been proved to remarkably affect the catalytic performance of catalysts at temperatures over 100°C [76,131,132], which, in this review, can be defined as an atmosphere effect. For example, Bashkova et al. [76] tested H_2S catalytic oxidation on NaOH modified activated carbons at 150°C using reformat as model fuel gas streams. They found that CO and CO_2 in challenge gas led to the formation of COS during the desulfurization process, decreasing the desulfurization efficiency. This atmosphere effect might also occur at room temperature.

Sithikhankaew et al. [111] explored the effect of CO_2 on the room temperature H_2S catalytic oxidation performance on KOH -modified activated carbon catalysts. The authors found that CO_2 reacted with KOH to generate K_2CO_3 or/and KHCO_3 during desulfurization and the

latter two species inhibited the reaction between KOH and H_2S , resulting in a decrease of the desulfurization efficiency. Interestingly, the H_2S removal performance on virgin activated carbon remarkably improved after the introduction of CO_2 , however, the authors did not explain this phenomenon. In our opinion, the increased performance might be related to the reaction of CO_2 with the carbon surface defects [133,134], altering the surface chemistry of activated carbon and providing some level of basicity. The negative role of CO_2 on the H_2S removal performance was found by Wang et al. [93], who studied the H_2S removal on polyethyleneimine-functionalized mesoporous carbon nanosheets. The decreased performance was ascribed to the reaction between CO_2 and polyethyleneimine, decreasing the amounts of the catalytic sites for H_2S catalytic oxidation. In addition, in both studies no COS was detected during the desulfurization process, which differ from the results obtained at temperatures higher than 100°C [76]. This might be attributed to the low reactivity of CO_2 with H_2S at room temperature.

The negative effect of CO_2 was clearly showed by the Badosz's group in their study of desulfurization of digester gas on catalytic carbons [113]. They found that commercial carbon catalysts enriched with a basic and relatively reactive phase, including alkaline earth oxide or caustics, reacted with CO_2 (especially when water was present) forming carbonates, which led to a premature exhaustion of the catalytic activity. A low capacity measured in these conditions could be also linked to the lack of oxygen supplied to the system.

The oxygen content in challenge gas was also a factor influencing the H_2S removal performance at mild temperature. It was found that small amount of oxygen is insufficient to allow H_2S full oxidation while excessive oxygen resulted in the formation of SO_2 , decreasing the sulfur selectivity of the catalysts [31,135]. Liu et al. [136] studied the effect of the oxygen content on the room temperature H_2S removal performance on Ce-Fe decorated activated carbon catalysts. The experimental results revealed that H_2S removal increased to a maximum with an increasing oxygen content in challenge gas and then kept almost constant even in the excessive oxygen concentration. However, the authors did not provide explanation for this behavior. Zhang et al. [28] reported that the needed oxygen content for room temperature H_2S oxidation on carbon catalysts is much higher than their stoichiometric ratio, in some cases even reaching a 30-fold excess of the stoichiometric amounts. The obtained results are different from those collected at mild-temperature and a high oxygen content needed at room temperature might be related to the slow kinetic of oxygen activation on the catalyst surfaces.

3.5. Carbon conductivity

Carbon conductivity represents their electron transfer ability, which generally depends on the texture, surface chemistry, and graphitization degree of carbonaceous materials [137]. It is well known that the electrical conductivity plays an important role in catalytic processes [138–140]. Therefore, in the case of H_2S catalytic oxidation, since this process involves an electron transfer, a high conductivity of a catalyst has been indicated as beneficial. In fact, in many cases it dictates the use of carbon-based materials as a support for various catalytic phases. The importance of this feature was first directly indicated by Badosz and coworkers [129], who investigated the H_2S removal on the composites of zinc(oxy)hydroxide with graphite oxide and graphene under ambient conditions. The authors found that the graphite oxide component was more beneficial than graphene was, since it provided oxygen-containing functional groups that formed chemical bonds with zinc(oxy)hydroxide phase. This helped with an electron transfer resulting in oxygen activation, thus promoting the oxidation of H_2S . The high conductivity of the composites was also suggested to advance the above process. A direct effect of these composites' features on the electrical conductivity was discussed in Ref. [141], where it was suggested that not only carbon in an sp^2 hybridization but also new bonds formed at a composite interface were responsible for their conductive behavior.

To further advance the H_2S removal from the gas phase, Badosz

et al. [142] used Au nanoparticles (AuNPs) to modify the zinc hydroxide/graphite oxide composites. The presence of graphite oxide increased the composites' surface structural and chemical heterogeneity, prevented the fast recombination of photo-generated electrons and holes during desulfurization, and also promoted the efficiency of the electron transfer favoring the formation of active oxygen species/superoxide ions. The incorporated AuNPs were also found to be responsible for the enhanced performance, since they increased the conductivity of the composites and promoted the electron transfer from the composites to oxygen. As a result, the composites presented a marked increase in the H_2S removal capacity compared to that on the zinc hydroxide and zinc hydroxide/AuNPs.

In another study of Bandosz et al. [143], they found that the formation of metallic copper species in composites of copper (hydro)oxychlorides with graphene or graphite oxides, besides the direct contribution of Cu species to oxygen activation [55] discussed above, was beneficial for H_2S oxidation, through an increase in the conductivity. Recently, Yang et al. [101] evaluated the effect of the support on the performance of the catalysts containing ZnFe_2O_4 as an active phase with activated carbon and silica as supports. Their results indicated that the carbon conductivity, besides other important features, contributed to the high catalytic activity (Fig. 10).

3.6. Speciation of the products

The predominant product of H_2S catalytic oxidation at room temperature is elemental sulfur. In some cases, the over-oxidation of H_2S or/and elemental sulfur resulted in formation of SO_2 , which was trapped by the micropores of carbon catalysts and eventually was converted to sulfuric acid or sulfates on the carbon surface. On the metal oxide-modified carbon catalysts, metal sulfides were also included in the products. Generally, the deposition of these sulfur-containing products on the carbon surface results in the deactivation of the catalysts.

Different from the abovementioned, Steijns et al. [144] found a positive role of elemental sulfur on the H_2S catalytic oxidation. They revealed that sulfur formed during desulfurization preferred to be trapped in the micropores of carbons with sizes below 1 nm, where it was converted into sulfur radicals, which play a catalytic role in H_2S catalytic oxidation. The autocatalytic role of elemental sulfur on H_2S oxidation was also indicated by Subrenat et al. [110], who studied the H_2S removal performance on activated carbon cloths. Their results suggested that the elemental sulfur played a catalytic role in H_2S oxidation under dry conditions, whereas, under moist conditions, this process did not take place owing to the formation of water film on the carbon surface. This finding is very interesting but either Steijns et al. [144] or Subrenat et al. [110] failed to further elaborate the mechanism of these catalytic actions.

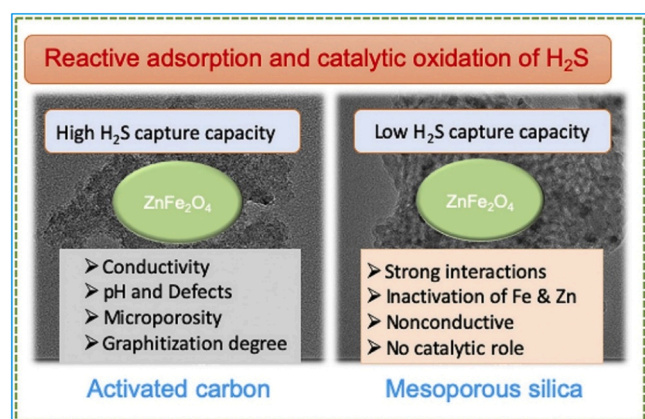


Fig. 10. The effect of support features on their desulfurization performance. Copyright 2020, Elsevier. Reprinted with permission from Ref. [101].

In another study, Wu et al. [145] proposed that sulfur radicals formed during desulfurization benefited dissociation of H_2S and activation of O_2 , thus promoting H_2S oxidation. As seen in Fig. 11, the authors suggested that in an initial reaction, the O_2 molecules were activated into $\text{O}_2^{\cdot-}$ on the carbon defects and then reacted with the dissociated HS^- forming elemental sulfur. With the duration of desulfurization, the carbon defect sites would be covered by bulky sulfur. In such a case, nitrogen-containing functional groups present on the carbon surface promoted the formation of sulfur radicals ($\text{N-C}(\text{S}_n)$), which captured O_2 and activated it into $\text{O}_2^{\cdot-}$. In addition, the sulfur radicals ($\text{N-C}(\text{S}_n)$) also could capture H_2S and resulted in its dissociation. Unfortunately, the authors did not prove the existence of these sulfur radicals.

Even though the autocatalytic role of elemental sulfur would be of great importance for H_2S oxidation, and could provide new insights on better understanding the whole oxidation process, the conclusions/hypothesis on its role at present are empirical, and the absence of a substantial evidence for the formation of the intermediate species made these conclusions even more feeble. More efforts are encouraged in the future to engage in this research direction.

4. Recent advances in H_2S catalytic oxidation on various carbonaceous materials

4.1. Activated carbon-based catalysts

Activated carbons are the most common carbonaceous materials that can be produced from diverse carbon sources through carbonization followed by an activation process. Their relatively low costs, high surface area, developed porosity and strong mechanical stability, allowed them to be extensively used as media for H_2S removal in a variety of industrial processes. Activated carbon not only can be used as a support to load metal oxides for the H_2S removal in an oxygen-free conditions [77,122,146–149], but also as a catalyst for H_2S oxidation in an oxygen-containing atmosphere [69,89,117]. While the performance of the former mainly relies on the chemical reactivity of specific metal oxides, the latter needs an O_2 concentration much higher than the stoichiometric ratio of H_2S oxidation [150]. Since this review focuses on the catalytic oxidation of H_2S at room temperature, the studies on the use of carbons as H_2S adsorbents or catalysts for selective catalytic oxidation are considered as being out of scope. It has been widely reported, and discussed above, that the H_2S catalytic oxidation performance of activated carbons used as catalysts can be remarkably improved after the modifications with the nitrogen species, alkaline media or/and metal oxides.

Yang et al. [102] were first to explore the ambient H_2S removal performance from moist air, via catalytic oxidation, on ZnFe_2O_4 modified activated carbon. The authors found that besides elemental S, the desulfurization products also included small amounts of sulfides and sulfates (Fig. 12a). This indicated that both catalytic oxidation and reactive adsorption were parts of the desulfurization mechanism. The H_2S removal capacity of the prepared catalysts reached 122.5 mg/g and was much higher than that of activated carbon without the modifications. The incorporated ZnFe_2O_4 not only provided an alkaline environment, triggered by hydroxylation, advancing H_2S catalytic oxidation on the carbon surface, but also supplied the active sites for H_2S oxidation. Moreover, FeOOH intermediates, formed during desulfurization were found as playing a catalytic role in H_2S oxidation. Similar results were also reported by Chen et al. [151], who evaluated the H_2S removal from moist air on CuFe_2O_4 modified activated carbon. Their results also indicated the formation of the FeOOH species which promoted oxidation of H_2S during desulfurization.

The synergistic effect between ZnFe_2O_4 and activated carbon advancing H_2S removal was revealed by Yang et al. [101] in their another study. The electron-rich matrix of the carbon phase and its abundant surface defects enhanced the transfer of electrons from the

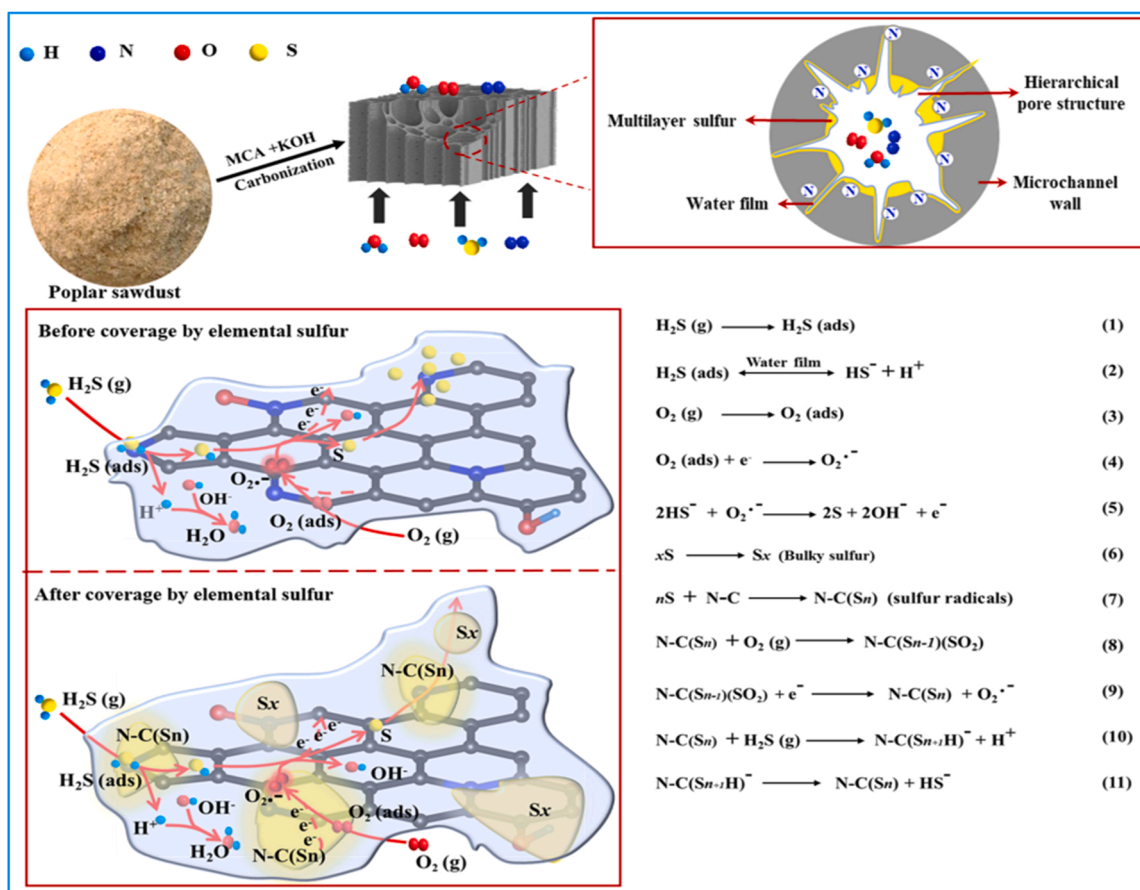


Fig. 11. Schematic illustration of the catalytic oxidation of H_2S on the NBACs. Copyright 2022, Elsevier. Reprinted with permission from Ref. [145].

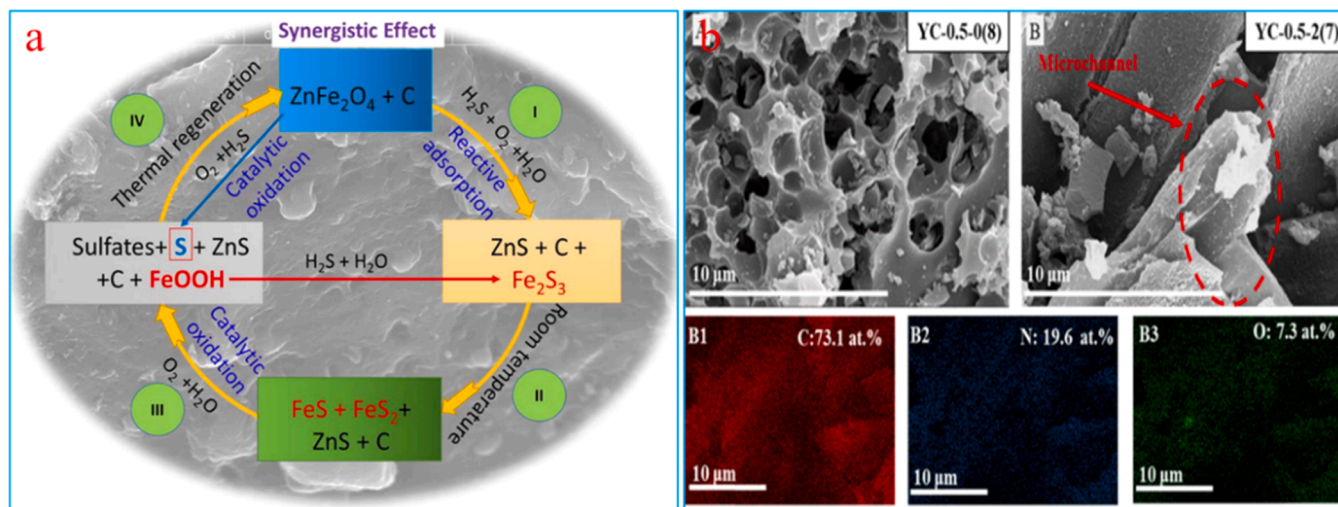


Fig. 12. (a) The reactive pathway of H_2S on $\text{ZnFe}_2\text{O}_4/\text{activated carbon}$ at a room temperature. (b) SEM images of YC-0.5-0(8) (A) and YC-0.5-2(7) (B), and its corresponding elemental mapping. (a) Copyright 2020, Elsevier [102]. (b) Copyright 2022, Elsevier [145].

carbon matrix to the adsorbed O_2 , thus promoting activation of O_2 and oxidation of H_2S . The authors indicated that the graphitization degree of activated carbon, its microporosity and surface pH also contributed to catalytic oxidation of H_2S . Interestingly, in their following study, Yang et al. [152] reported that visible light exposure would inhibit H_2S removal on ZnFe_2O_4 -modified activated carbon, both in both moist and

dry conditions. It is because light led to the generation of electron-hole pairs on ZnFe_2O_4 , which resulted in the formation of $\bullet\text{OH}/\text{O}_2^{\cdot-}$ species with a strong oxidative capability converting H_2S into sulfates, not to the desired elemental S. The formed species readily blocked the pores of the catalysts and caused their deactivation.

Siriwardane et al. [153] synthesized MgO impregnated granular

activated carbon composites using a spray technique. In their approach nano magnesium oxide was incorporated to the micropores of activated carbon. The H₂S breakthrough tests' results indicated that both physical adsorption and catalytic oxidation occurred on the composites during desulfurization process and the latter was predominant. The authors suggested that MgO not only provided active centers for H₂S oxidation, but also reactive sites for H₂S chemisorption. A different view was presented by Yang et al. [77] and Cepollaro et al. [154], who suggested that MgO has no reactivity towards H₂S at room temperature. According to them, its advancement effect on the H₂S removal resulted from its basicity bringing an alkaline environment for H₂S dissociation. This result was further confirmed by Xu et al. [155], who simulated the reaction pathway of desulfurization on MgO/graphene oxide composites using DFT calculation methods. The authors found that the direct reaction of HS[−] with MgO to form MgS needs a Gibbs free energy (ΔG) of 0.853 eV, while the needed ΔG for HS[−] oxidation by O₂[−] radicals into elemental sulfur is only − 0.174 eV. This result strongly indicated that H₂S on MgO/rGO preferred to be catalytically oxidized into elemental sulfur rather than directly react with MgO forming MgS through an acid–base reaction.

Besides monometallic oxides, bimetallic oxides have been also considered as the prospective modifiers of activated carbons for the efficient H₂S removal through catalytic room temperature oxidation, owing to a synergistic effect they provided [100]. For example, Liu et al. [136] studied H₂S catalytic oxidation on Ce-Fe impregnated activated carbon, and found that the ability of CeO₂ to store oxygen and release it promoted oxidation of Fe²⁺ to Fe³⁺ during desulfurization, which remarkably increased the catalytic activity of the catalysts and also decreased the demand for O₂ as a needed component for H₂S oxidation.

In intensified efforts to explore efficient modification strategies, various new types of activated carbons were prepared to advance the H₂S removal. For examples, Kante et al. [156] prepared series of spent coffee-based activated carbons using zinc chloride as an activation agent. Caffeine-originated inherent nitrogen groups on the carbon materials plus the large volumes in pores with sizes between 1 nm and 3 nm resulted in the H₂S removal of 127 mg/g, with elemental sulfur as a predominant product. Nowicki et al. [120] found that the activated carbons obtained from coffee industry waste materials exhibited the excellent H₂S removal capacity of 281.5 mg/g owing to their alkaline surface features and the presence of the large amounts of a mineral matter in their matrix. Cattle manure was used as a precursor by Tuerhong et al. [157] to prepare activated carbon through various activation methods. The authors found that carbons activated with CO₂ showed the H₂S removal capacity of 868.45 mg/g, much higher than those steam activated (62.95 mg/g). The catalytic oxidation products included elemental sulfur, sulfates/sulfuric acid and sulfites/sulfonic acids, which indicated the complexity of the catalytic process. The developed microporosity, basic surface pH along with the self-catalytic role of intrinsic sulfur were responsible for the excellent performance. The authors considered that as-received activated carbons were promising alternatives for the catalytic H₂S removal owing to their high efficiency and low cost estimated as 1.05 \$/ kg.

In another study, Wu et al. [145] prepared N-doped biomass derived activated carbons (NBAC) in a one-step pyrolysis using supramolecular melamine cyanurate as a nitrogen source and poplar sawdust as a carbon source. The obtained carbon materials had a very high N content of 19.6 at% and possessed a microchannel structure (Fig. 12B). The former provided massive active sites for H₂S catalytic oxidation, while the latter promoted the mass transfer of reactants and the migration of produced elemental sulfur to form a multilayer sulfur deposit. As a result, the H₂S removal capacity on NBAC was as high as 1872 mg/g. An important benefit of this study is that it provides an interesting alternative for the preparation of nitrogen doped carbons with a high nitrogen density, what is considered as a challenge in this field.

Table 2 summarizes the H₂S removal capacities on activated carbons with different modification strategies, where marked differences on

Table 2H₂S removal capacity on activated carbons with different modifications.

Sample	Feed gas composition	C _{outlet} H ₂ S (ppm)	H ₂ S removal capacity (mg/g)	Ref.
ZnFe ₂ O ₄ /activated carbon	1000 ppm H ₂ S, moist air, RH= 70 %	100	170.1	[101]
MgO/activated carbon	10,000 ppm H ₂ S, moist air, RH= 80 %	50	275	[153]
CuFe ₂ O ₄ /activated carbon	10,000 ppm H ₂ S, moist air, RH= 80 %	0	667	[151]
Cu _{0.5} Zn _{0.5} O/activated carbon	2500 ppm H ₂ S and O ₂ , moist N ₂ , RH= 50 %	2500	118.0	[158]
5Ce-20Fe/activated carbon	450 ppm H ₂ S, 10 O ₂ , moist N ₂ , RH= 80 %	0	820	[136]
Coffee waste based activated carbon	1000 ppm H ₂ S, moist air, RH= 70 %	100	281.5	[120]
Cattle manure-based activated carbon	1200 ppm H ₂ S, 0.8 % O ₂ , N ₂ , prehumidified 8 h	100	868.45	[157]
N-modified activated carbon	500 ppm H ₂ S, 5000 ppm O ₂ , moist N ₂ , RH= 80 %	25	1827	[145]

their performance were observed. These differences might be related to the nature of impregnated metal oxides, surface chemistry, textural properties of activated carbons and the operation conditions. Compared to the N-modified activated carbon catalysts, metal oxides modified ones have the relatively worse H₂S removal performance. This inferior performance might be linked to the reactivity of metal oxides with H₂S, which deteriorates the alkaline environment and decreases the population of active sites needed for H₂S catalytic oxidation.

4.2. Mesoporous carbon-based catalysts

Owing to the deposition of sulfur-containing products on the carbon surface, micropores of carbonaceous materials are readily clogged in the desulfurization process, thereby providing one path of a catalyst deactivation. Mesoporous carbons, on the other hand, have large interparticle and intraparticle pores [59,81,135], which provide abundant space for the sulfur deposition, thus further improving the H₂S removal performance. To this end, various mesoporous carbons have been prepared and their H₂S catalytic removal performances have been studied in detail.

Long et al. [91] synthesized nitrogen-rich mesoporous carbons via a colloidal silica-assisted sol–gel process using phenol, melamine, and formaldehyde as precursors (Fig. 7a). Their nitrogen content and speciation could be regulated by varying the molar ratio of melamine to phenol and also by changing a carbonization temperature. The H₂S removal capacity reached 2770 mg/g when the N content was 10 wt%. The high volume of mesopores and the abundant nitrogen groups, especially the pyridine-type ones, were indicated as responsible for these carbons' excellent performance in H₂S oxidation. The pyridine-type groups provided basic sites for H₂S dissociation and also acted as specific sites for oxygen activation. These conclusions follow the importance of the governing factors, discussed in the first part of this review.

Recognizing the importance of the pore volume and N-doping for room temperature H₂S catalytic oxidation, mesoporous carbon catalysts can be fabricated using various methods and those studied for gas phase desulfurization focused on achieving the high catalytic performance. For examples, Yu et al. [159] used microporous Zn-based zeolitic imidazolate framework (ZIF-8) polyhedrons as a carbon precursor and prepared two-dimensional N-doped mesoporous carbon nanosheets via a molten salt method. Jiang et al. [160] prepared nitrogen-doped porous carbon

from waste polyurethane foams as a precursor using hydrothermal carbonization and K_2CO_3 high temperature activation. In another study, Jiang et al. [161] used cypress sawdust and carbon nitride as carbon and nitrogen precursors, respectively, with K_2CO_3 as an activation agent. The H_2S removal capacities on these carbon materials, some extraordinary in their extent, are summarized in Table 3.

Long et al. [162] developed alkaline mesoporous carbons catalysts through a simplified silica templating method. The authors integrated template etching and an alkaline modification of a carbon matrix into a single step. The mesopores in the carbon matrix were formed by NaOH etching the silica template, and they were partially filled with the NaOH solution, owing to the absence of any washing. The target porosity and basicity of the catalysts could be simultaneously adjusted by regulating the etching degree and also the organic/inorganic ratio. On such materials, the highest H_2S removal capacity reached 2650 mg/g. In their following study, Long et al. [72] prepared mesoporous carbon spheres (MCSs) in a kilogram-scale using a suspension assisted nanocasting method, and after caustic impregnation used those MCSs as catalysts for H_2S oxidation. The authors compared the H_2S catalytic performance on MCSs impregnated with Na_2CO_3 , NaOH, K_2CO_3 , MgO and KOH, and they found that MgO containing MCSs exhibited the highest H_2S removal capacity of 2460 mg/g. The low solubility of MgO in the water film resulted in a continuous release of OH^- , which facilitated H_2S dissociation for a long time and thereby extended the H_2S breakthrough time, as previously suggested by Badosz et al. [47] in their analysis of Midas® catalytic carbon. In another study, Long et al. [71], prepared two dimensional mesoporous CaO/carbon hetero-structured catalysts synthesized through a one-step carbonization of calcium gluconate. The catalysts presented a 2-D nanosheet structure in a micrometer scale, with a CaO content of about 50 wt%. This active phase was highly dispersed on the nanosheets with an average size of about 15 nm (Fig. 13 (b, c, d, e, f)). Owing to the developed mesopores and highly dispersed CaO nanoparticles, the 2D CaO/carbon heterostructured catalysts achieved the ultrahigh H_2S removal capacity of 9100 mg/g. To our best knowledge, this is the highest H_2S removal capacity that have been reported at a room temperature up to now.

Different from Long's work, Wang et al. [93] used graphene oxide nanosheets as a structure-directing agent and colloidal silica as a hard template to synthesize mesoporous carbon nanosheets via aqueous

solution chemistry. After a polyethyleneimine (PEI) modification, these mesoporous carbon nanosheets were used as catalysts for the H_2S removal. They had a two-dimensional lamellar structure and an interconnected mesoporous framework. The highly dispersed PEI provided the abundance of amine groups promoting the dissociation of H_2S . The above advantages resulted in the H_2S removal capacity of 465 mg/g.

Florent et al. [163] added Pluronic surfactant F127 to sewage sludge to prepare mesoporous carbon-based desulfurization media through a simple pyrolysis at 950 °C, at two heating regimes. The introduction of F127 increased a carbon content and the volumes of mesopores in the catalysts, while a slow pyrolysis rate improved the structural order of the carbon phase and enhanced the dispersion of the catalytic inorganic phase (CaO , MgO , Fe_2O_3) inherent in sludge. These alterations also facilitated an electron transfer, thus promoting the catalytic oxidation of H_2S and significantly increasing the desulfurization performance.

4.3. Carbon nanotubes-based catalysts

Carbon nanotubes (CNTs) are sp^2 hybridized carbon materials with a high aspect ratio (~ 1000) and a morphology of hollow cylindrical tubes [164,165]. Based on the numbers of graphite layers (Fig. 14a) they can be divided into single-walled nanotubes (SWNTs), double-walled nanotubes (DWNTs), and multi-walled nanotubes (MWNTs) [165]. Due to their superior physiochemical properties, such as hollow and layered structures, a high stability and conductivity, moderate surface area and porosity, π -conjugative structures, and curvature of sidewalls, CNTs have also been selected as potential media for the H_2S removal through catalytic oxidation at room temperature.

Chen et al. [166] studied the H_2S removal performance of Na_2CO_3 impregnated CNTs and explored the influence of the CNT structure on it. The experimental results indicated that the H_2S removal capacities on SWNTs were much greater than those on MWNTs. Moreover, their performance decreased with increasing the tube diameter. The authors suggested that the inherent heteroatoms or surface defects in a CNTs matrix acted as active sites for oxygen activation, and the Na_2CO_3 impregnant enhanced the hydrophilicity and basicity of CNTs (Fig. 14b). As a result, the excellent H_2S removal capacity of 1510 mg/g was achieved on these catalysts, and the oxidation products were elemental sulfur and sulfates. Rashidi et al. [167] compared the H_2S removal performance on allylamide-grafted MWCNTs and on oxidized MWCNTs. The former exhibited the higher capacity than the latter owing to the presence of amine groups, which provided the alkaline environment for H_2S dissociation and also acted as active sites for chemisorption of H_2S . Ji et al. [168] tested the H_2S removal performance on MWCNTs decorated with hydrated ferric oxide (HFO). The highly dispersed HFO nanoparticles and formed Fe-O-C bonds contributed to their high H_2S removal capacity of 144.2 mg/g. The former led to an increase in an active sites exposure, while the latter promoted an electron transfer between MWCNTs and HFO, important for the desulfurization process.

4.4. Graphite oxide and graphene-based catalysts

Graphite oxide is a layered carbonaceous material with an AB stacking order and enriched diverse oxygen-containing functional groups on its surface [169]. These groups include epoxy, hydroxyl, carboxyl and carbonyls and they make graphite oxide dispersible in water, which brings the possibility to fabricate various composite materials with its involvement [170]. Graphite oxide attracted much attentions since it was established as a precursor for making graphene. The latter has a monolayer structure with a high contribution of sp^2 hybridized carbon atoms [171–173]. Owing to a physical and chemical stability, electron mobility and heat transfer, both graphite oxides and graphene have been used as media for H_2S removal [174], and their H_2S removal capacities are compared in Table 4.

Badosz and coworkers explored the H_2S removal performance on series of graphite oxide composites with various metal (hydr)oxides,

Table 3
 H_2S removal capacities on various mesoporous carbon catalysts.

Sample	Feed gas composition	C_{outlet} H_2S (ppm)	H_2S removal capacity (mg/g)	Ref
M/P-2	1000 ppm H_2S , moist air, RH= 80%	5	2770	[91]
NMCS-50–8–20%	1000 ppm H_2S , 2 % O_2 , moist N_2 , RH= 70 %	250	1370	[159]
KHC-1	1000 ppm H_2S , air, moist N_2 ,	1000	205.1	[160]
NPC-1	1000 ppm H_2S , 1 % O_2 , moist N_2 , RH= 30 %	50	426.2	[161]
AMC-0.5 – 10%	1000 ppm H_2S , 1 % O_2 , moist N_2 , RH= 80 %	50	2650	[162]
MCS-MgO-15	1000 ppm H_2S , 1 % O_2 , moist N_2 , RH= 80 %	50	2460	[72]
2D CaO/carbon heterostructures	1000 ppm H_2S , 1 % O_2 , moist N_2 , RH= 80 %	50	9100	[71]
MCNs-PEI-25	1000 ppm H_2S , 1 % O_2 , moist N_2 , RH= 80 %	50	465.1	[93]
B-F-950-S	1000 ppm H_2S , moist air, RH= 70 %	100	221.2	[163]

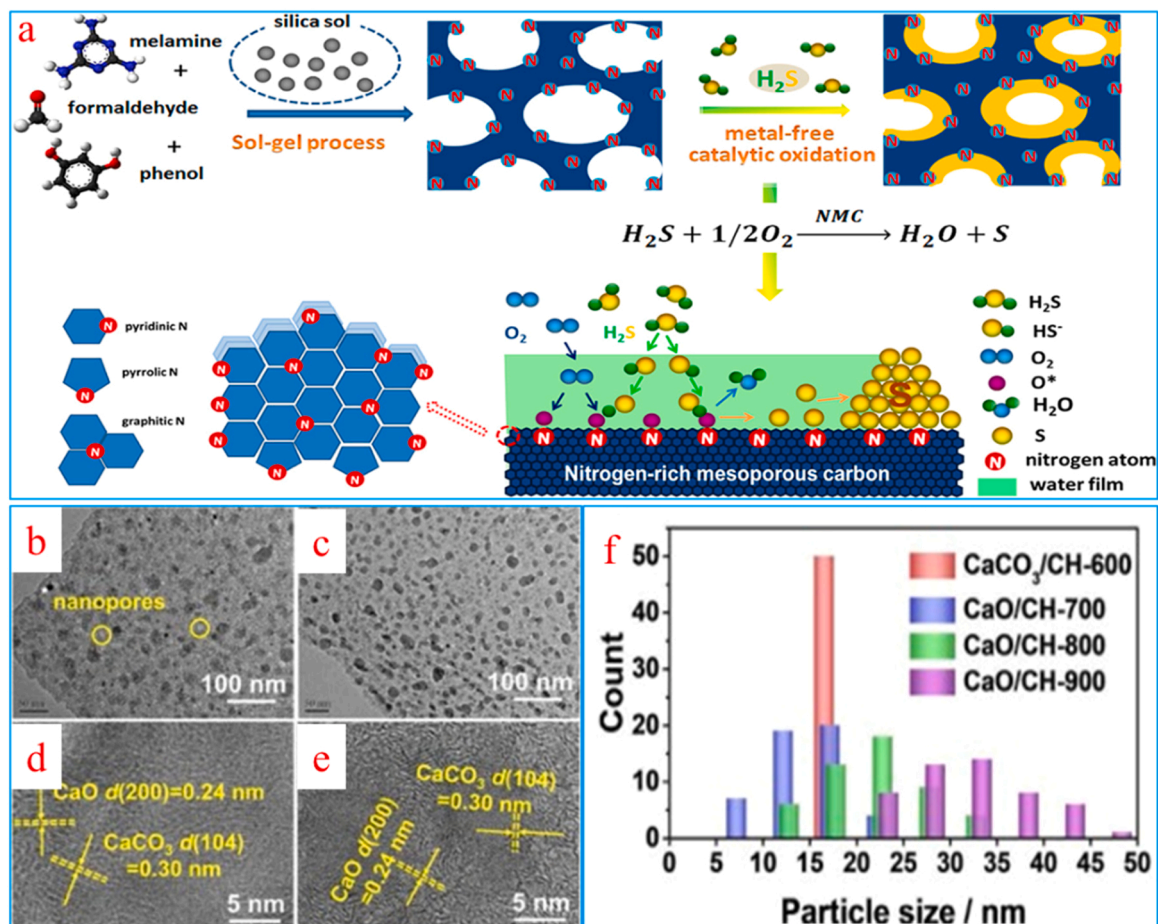


Fig. 13. (a) Schematic fabrication of NMC for the direct oxidation of H_2S and the possible reaction process. TEM images of the CaO/CH-700 (b, d), CaO/CH-800 (c, e), and the particle size distribution diagram.

(a) Reprinted with permission from Ref. [91] Copyright 2013, American Chemical Society (f). Copyright 2021, Elsevier [71].

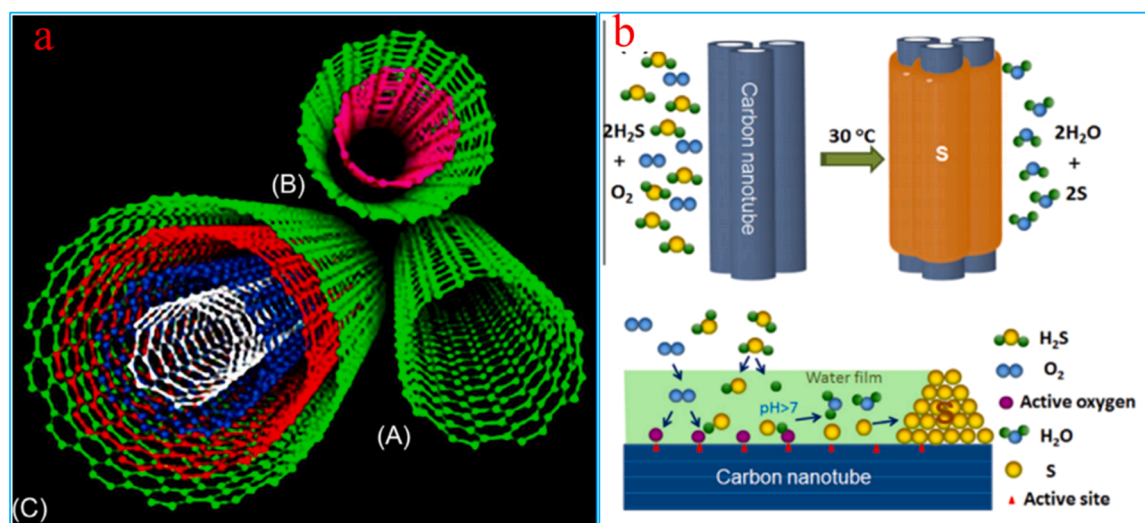


Fig. 14. (a) Single-walled carbon nanotubes (SWCNTs) (A), double-walled carbon nanotubes (DWCNTs) (B), and multi-walled carbon nanotubes (MWCNTs) (C). The schematic representation of H_2S oxidation over the alkaline CNTs.

(a) Copyright 2019, Elsevier. [165]. (b) Copyright 2011, Elsevier. [166]

including Co, Zr, Zn, Cu, Cd [103,129,142,170,175–178]. The modifications increased the H_2S removal through a synergistic effect. While the introduced metal (hydr)oxides were found to promote H_2S oxidation

and simultaneously participated in the reactions with H_2S , graphite oxide contributed to an electron transfer and oxygen activation. Although the synthesized composites presented different performance

Table 4
H₂S removal capacities on graphite oxide/graphene based catalysts.

Sample	Feed gas composition	C _{outlet} H ₂ S (ppm)	H ₂ S removal capacity (mg/g)	Ref
CoGO-5	1000 ppm H ₂ S, moist air, RH= 75%	100	120.3	[170]
CoOOH- GO10	1000 ppm H ₂ S, moist air, RH= 80%	100	108.2	[175]
AuZnGO	1000 ppm H ₂ S, moist air, RH= 75%	100	154.7	[142]
M-GO10	1000 ppm H ₂ S, moist air, RH= 70%	100	114.8	[103]
Cd(OH) ₂ - GO10	1000 ppm H ₂ S, moist air, RH= 80%	100	83.3	[178]
ZnGO-20	1000 ppm H ₂ S, moist air, RH= 75%	100	155	[176]
ZrG-1	1000 ppm H ₂ S, moist air, RH= 70%	100	52.8	[177]
ZnGO- EPM	1000 ppm H ₂ S, moist air, RH= 75%	100	211.6	[129]
ZnGr-EPM	1000 ppm H ₂ S, moist air, RH= 75%	100	149.7	[129]
CuGr-EPM	1000 ppm H ₂ S, moist air, RH= 70%	100	159.8	[143]
AGA-30%	1000 ppm H ₂ S, 1% of O ₂ , moist N ₂ , RH= 80%	50	3190	[179]

owing to the differences in their composition, surface chemistry and heterogeneity level, the desulfurization products were similar and included elemental S, metal sulfides and sulfates.

Compared to graphene, graphene oxide contains more oxygen-containing groups and structural defects [180], which could promote oxygen activation, thus improving the H₂S catalytic oxidation performance. Pan et al. [179] studied the H₂S removal performance on three dimensional Na₂CO₃ impregnated graphene aerogels, which were prepared by a hydrothermal process followed by impregnation with a Na₂CO₃ solution. As seen in Fig. 15, aerogels with an interconnected three dimensional graphene network were formed by the self-assembly of ultra-thin and highly dispersed graphene flakes after the treatment with the Na₂CO₃ solution (Fig. 15(c, f)). Interestingly, this structure was not formed in the absence of Na₂CO₃ (Fig. 15(b, e)). It was proposed that carbonates acted as cross-linking agents, binding and joining the graphene sheets, and the surface oxygen-containing groups improved the dispersion of carbonates throughout the graphene sheets by hydrogen bonds. However, an excessive Na₂CO₃ loading resulted in the formation of rod-like structures inhibiting the formation of the three-dimensional graphene network (Fig. 15(d, g)). Prepared aerogels exhibited the outstanding H₂S removal capacity of 3190 mg/g at room temperature. During the desulfurization process, the graphene sheets acted as electron donors activating O₂ molecules into superoxide radicals (O₂^{•−}), and the Na₂CO₃ species provided an alkaline environment for dissociation of H₂S into HS[−]. In addition, the interconnected macropore-structured graphene network ensured the accessibility of the H₂S molecules to the catalytic centers and provided a large storehouse for the formed

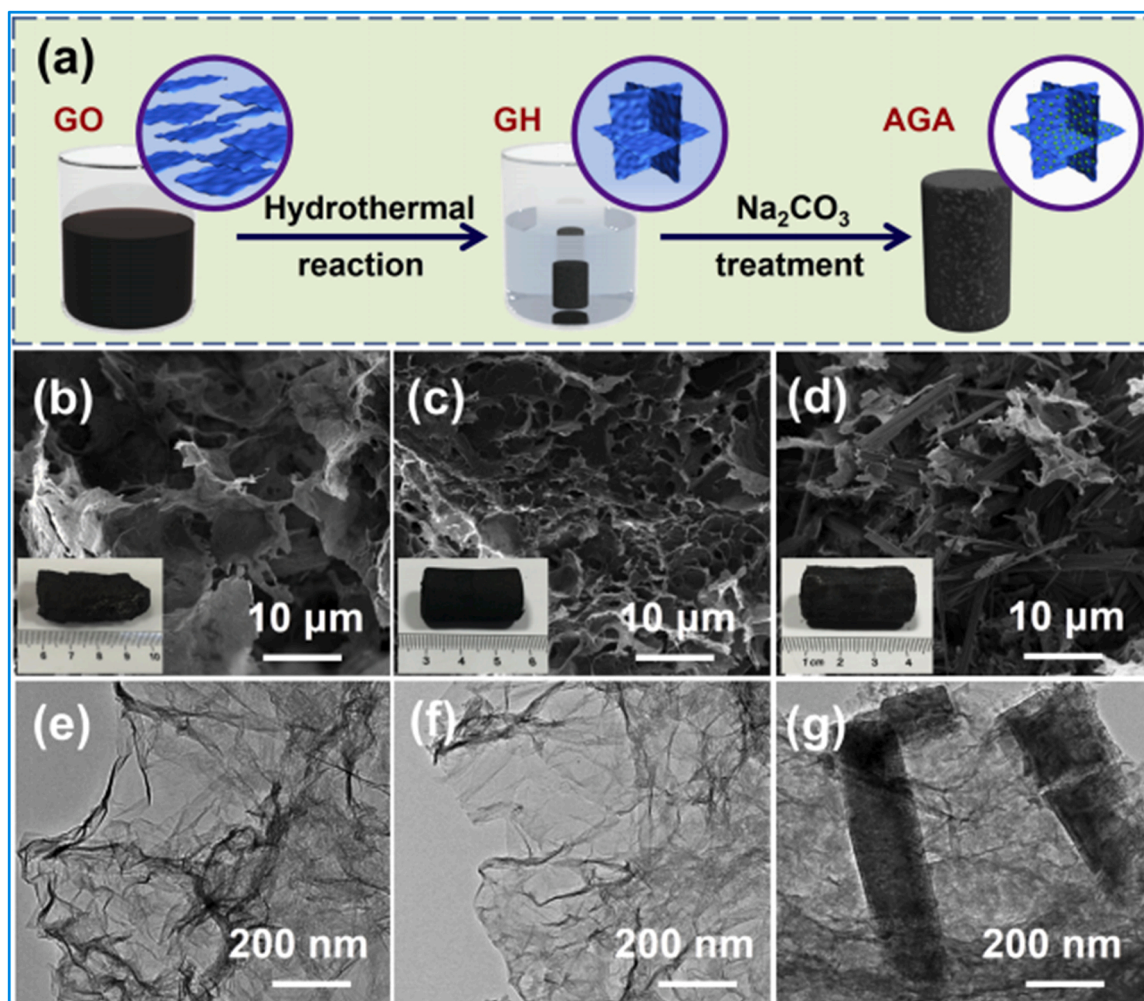


Fig. 15. (a) Schematic fabrication process of the AGAs; SEM images of (b) AGA-0, (c) AGA-30%, and (d) AGA-75%; TEM images of (e) AGA-0, (f) AGA-30%, and (g).

oxidation products.

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4.5. Carbon fiber-based catalysts

Carbon fibers with a diameter ranging from tens of nanometers to tens of micrometers, are classified into carbon nanofibers (CNFs, diameter $<1\ \mu\text{m}$) and carbon microfibers (CMFs, diameter $>1\ \mu\text{m}$) [181, 182]. Both of them can be fabricated by a melt-spinning process or a chemical vapor deposition process [183]. The carbon fibers present excellent properties including a high electrical conductivity, good mechanical strength, flexibility, and tunable structure. These features made them attractive candidates as media for the H_2S removal [184–187].

Sun et al. [188] synthesized a series of nitrogen-rich hierarchical

porous carbon nanofibers (N-PCNFs) through an electrospinning method followed by carbonization and an activation strategy. They used polyacrylonitrile (PAN) and zeolitic imidazolate (ZIF-8) as carbon and nitrogen precursors, respectively. The prepared materials were used as media for H_2S catalytic oxidation at room temperature. As seen in Fig. 16a, the carbonization temperature of the catalysts remarkably affected their H_2S removal performance. This is because it greatly influenced the nitrogen content and its configuration (Fig. 16b). The catalyst carbonized at $800\ ^\circ\text{C}$ showed the highest H_2S removal capacity of $1840\ \text{mg/g}$, ascribed to its high content of doped nitrogen and the abundant micropores and mesopores in the nanofibers. Here the doped nitrogen provided basic sites for H_2S dissociation, the micropores offered the developed specific surface area for the utilization of more active sites, and mesopores gave space for more elemental sulfur to be stored.

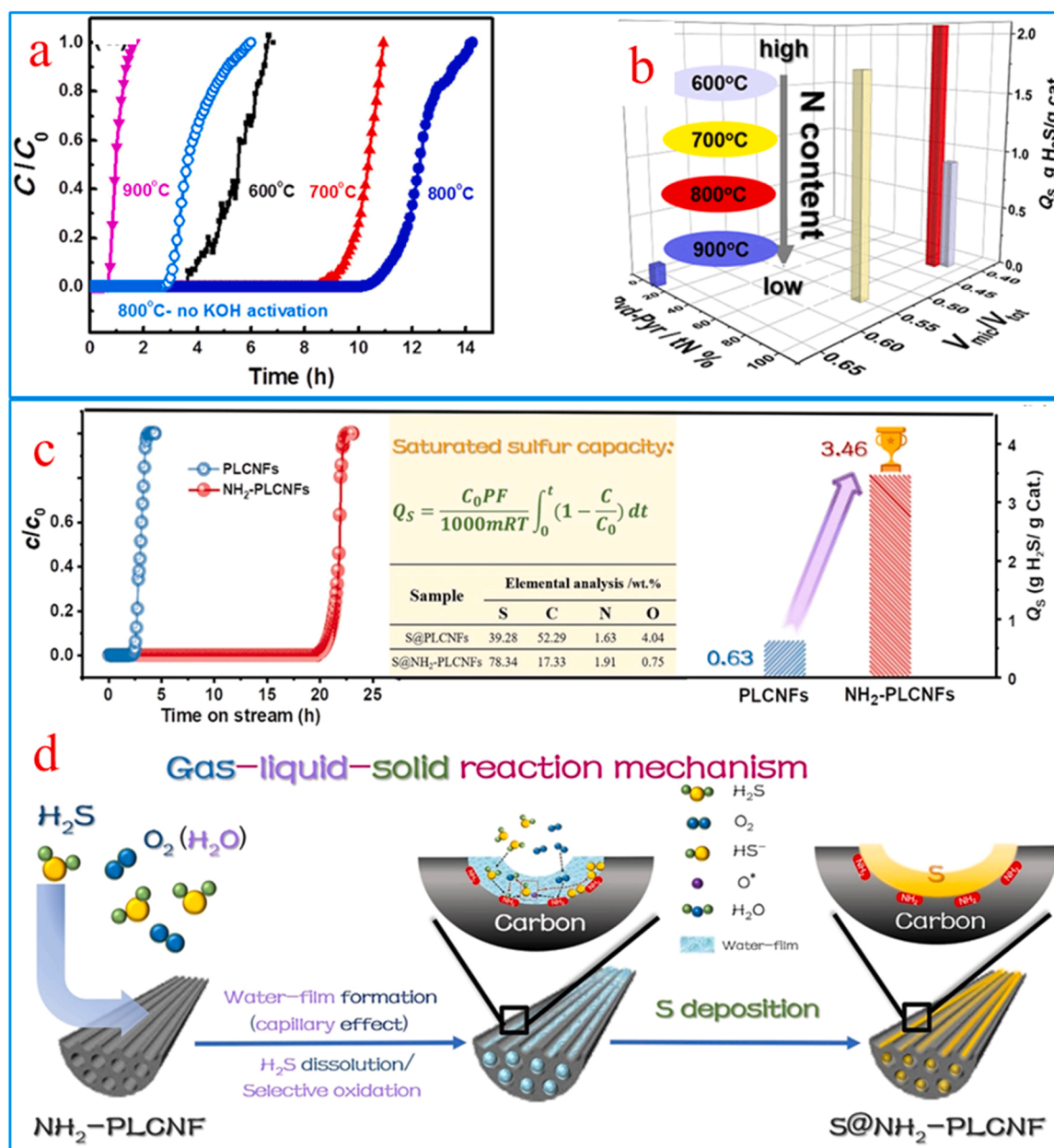


Fig. 16. H_2S breakthrough curves of N-PCNFs catalysts and the relationship between the saturated sulfur capacities (a), the ratio of pyd-pyr/ t_N (the relative ratio of pyridinic-N and pyrrolic-N content to the total nitrogen content in samples) and the ratio of $V_{\text{mic}}/V_{\text{tot}}$ of samples (b) Desulfurization performance of NH_2 -PLCNFs and PLCNFs (c), and the schematic illustration of the mechanism for H_2S selective oxidation over NH_2 -PLCNFs.

(a) Reprinted with permission from Ref. [188] Copyright 2019, Elsevier (b) Reprinted with permission from Ref. [94]. Copyright 2022, John Wiley and Sons

In their another study, Sun et al. [94] fabricated amino-functionalized lotus root-like carbon nanofibers (NH₂-PLCNFs) as a medium for H₂S catalytic oxidation. The grafted-NH₂ groups not only acted as Lewis-base sites facilitating dissociation of H₂S, but also enhanced the electron-donating ability of the carbon nanofibers to form active oxygen species. As a result, the as-prepared catalysts removed 3460 mg of H₂S/g (Fig. 16c). Based on the collected results, the authors proposed an H₂S oxidation mechanism on their material. As seen in Fig. 16d, moisture in feed gas formed the water-film in the interior nano-channels of NH₂-PLCNFs; following that, the H₂S molecule dissolved in that water film reacted with -NH₂ to form HS⁻ and -NH₃⁺, the dissolved O₂ molecules dissociated into the active oxygen species (O*) on the catalytic sites of the carbon surface, formed HS⁻ reacted with O* to produce elemental S and OH⁻, the former was stored in the channels of the catalysts, and the latter was captured by -NH₃⁺ to regenerate -NH₂ and H₂O. This process was ongoing until the channels of the catalysts were filled with elemental S.

Coelho et al. [189] studied H₂S removal on NiS₂ modified carbon nanofibers. Their nanofibers were synthesized by a catalytic decomposition of ethane on a graphite felt substrate. Therein NiS₂, as an active phase, donated one electron to O₂ to activate it, promoting catalytic oxidation of H₂S. In this study the strong hydrophobicity of the carbon nanofibers was considered as an important factor influencing the H₂S removal efficiency. The authors suggested that the hydrophobicity of the carbon nanofibers enabled condensed water to bring the sulfur particles deposited on NiS₂ out of nanofiber tangles, which allowed a continuous accessibility of active sites during the desulfurization process. Although this suggestion is interesting, the explanation of how water could bring the sulfur particles to the hydrophobic surfaces was not provided. In addition, the authors also indicated that the absence of ink-bottle pores in the nanofibers, plus their large surface area and external void volume also contributed to efficient H₂S oxidation.

5. Mechanisms of H₂S oxidation on carbon catalysts at room temperature

We need to point out that although the H₂S oxidation mechanism on different carbon materials is governed and influenced by the same factors, various targeted modifications lead to various levels of the advancement in the catalysts' performance, as discussed above. Here we aim to summarize this H₂S oxidation mechanism as a general one applied to all carbon-based catalysts active in the room temperature oxidation process. As indicated above, the catalytic oxidation of H₂S on the carbon materials is a complex process, which broadly includes

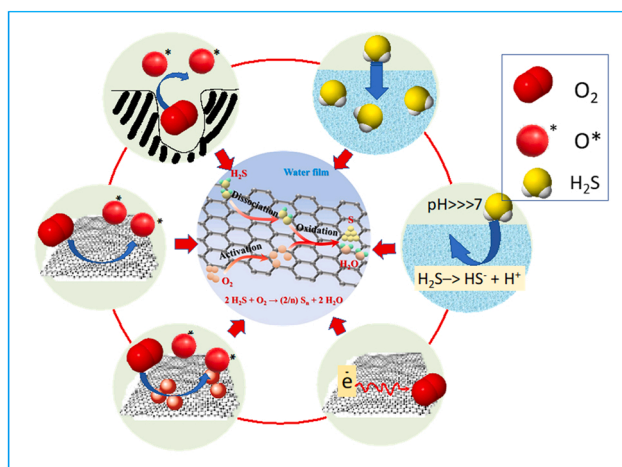
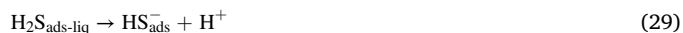


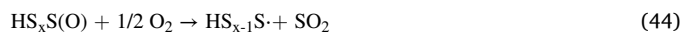
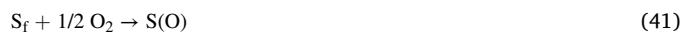
Fig. 17. Combination of factors leading to efficient carbon-based H₂S oxidation catalysts at room temperature. Red arrows indicate the contribution of each process to the overall H₂S catalytic oxidation mechanism.

diffusion of the H₂S molecule into the pore system, its dissociation and the O₂ activation on the carbon surface, oxidation reactions of HS⁻ and a product storage (Fig. 17). Specifically, the H₂S and O₂ molecules are firstly attracted to a carbon surface through adsorption; then adsorbed H₂S dissociates into HS⁻ and moisture in feed gas promotes this process. Upon the formation of the water film on the carbon surface, H₂S dissolves there and dissociates; adsorbed O₂ are transformed into active oxygen species on the active sites of carbon (defects, ultramicropores, heteroatoms, Cu species); HS⁻ ions are oxidized either to elemental sulfur or/and to SO₂ by these active oxygen species. In addition, a small amount of elemental sulfur is also further oxidized into SO₂ and it results in the formation of sulfuric acid with the involvement of oxygen and water. The reactions are as follows [52,69,70,190]:



where the gas, liquid and ads suffixes correspond to the species in gas, liquid, and adsorbed phases, respectively; C_f represents the carbon active sites participating in O₂ activation to O*.

In some cases, a different mechanism based on a free radical theory was proposed by researchers using elemental sulfur, S_x, polysulfides or/and HS_xSH as active sites for H₂S oxidation. The involved reactions are as follows [47,75,144,191]:



where S_f indicates sulfur-based active sites for O₂ activation or/and dissociation, and S(O) represents the sulfur sites with chemisorbed oxygen.

In very recent studies, in the desulfurization process researchers detected the formation of O₂^{·-} on the surface of carbon catalysts, using an electron paramagnetic resonance (EPR) analysis [48,71,179]. Therefore, a new H₂S oxidation mechanism based on this finding was proposed. Therein the O₂ molecule was activated into O₂^{·-} on the carbon active sites (ultramicropores, defects, heteroatoms), and dissociated HS⁻

was oxidized by $O_2^{\cdot-}$ to form elemental S deposited on the carbon surface. The involved reactions are as follows [71]:



where C_{AS} indicates the carbon active sites for O_2 activation.

6. Stability and durability of the carbon-based catalysts

As mentioned above, with the duration of the catalytic process, the sulfur-containing products of H_2S oxidation and surface reactions deposited on carbon result in the pore blockage and in the alterations of surface chemistry, thus causing deactivation of the catalysts. The exhausted catalysts would be treated as solid waste, sometimes hazardous one when pH is low, if they cannot be reused or regenerated, which could remarkably increase desulfurization costs in practical applications. Therefore, the regeneration performance of the carbon-based catalysts is also an important indicator for assessing the desulfurization performance. To address this, various regeneration methods were explored.

The regeneration process on an industrial scale was patented by Calgon Carbon [192]. On their catalyst- nitrogen- containing Centaur®, H_2SO_4 is the main product of surface reactions and to remove it and thus to reuse carbon, washing with suitable amounts of water at temperatures less than 100 °C was proposed.

Adib and Bandoz [193] studied the feasibility of water regeneration of the exhausted un-impregnated activated carbons. They found that the regeneration performance depended on the speciation of the oxidation products. The water-soluble sulfur oxides were totally washed out as sulfuric/sulfurous acid while the insoluble bulky sulfur polymers remained on the surface. The regeneration results indicated that a 30% recovery in the capacity of carbons could be achieved after water washing. In another study of the Bandoz's group [194], the H_2S removal performance of exhausted and regenerated coconut shell-based activated carbon, using cold and hot water washing, was analyzed. It was reported that the regeneration efficiency of the catalysts was slightly higher with hot water washing. This performance was linked to the capability of hot water to remove/oxidize some amounts of elemental sulfur from the carbon pore system.

Different from water regeneration, thermal regeneration was also used to recover the catalytic performance of the H_2S oxidation catalysts. Bagreev et al. [195] studied the thermal regeneration of spent coconut shell-based activated carbon by its heating in an air atmosphere at 300 °C. The authors found that this regeneration process could totally remove sulfur dioxide and elemental sulfur, thus the pore structure of the catalysts was recovered in 100%. Although good results were obtained in this study, it must be kept in mind that the regeneration temperature should be moderate since carbon materials combust in the oxygen enriched atmosphere at a high temperature.

In order to avoid the above problem, thermal regeneration in an inert atmosphere, as an alternative, was explored. For examples, Yang et al. [102] regenerated the exhausted $ZnFe_2O_4$ /activated carbon catalysts in a N_2 atmosphere at 500 °C for 2 h. The regeneration results indicated that the catalyst was almost totally regenerated and used in at least three cycles. Similar results were also obtained by Chen et al. [151], who regenerated the exhausted $CuFe_2O_4$ /activated carbon catalysts in a N_2 atmosphere at 500 °C for 2 h. Considering the solubility of SO_4^{2-} in water, Chen et al. [161] proposed a two-step method. The authors scrubbed the exhausted catalysts with hot water to remove SO_4^{2-} stored in the catalysts, and then heated the catalysts in a N_2 atmosphere at 400 °C for 1.5 h. Their results indicated that the H_2S removal capacity of the catalysts was recovered in about 86% even after five successive regeneration cycles. These limited examples indicate the excellent stability and durability of the carbon-based catalysts provided that a suitable regeneration method was selected.

7. Conclusions and perspectives

Recently, efficient H_2S removal became an important topic owing to increased interests in alternative energy sources, such as biogas, and in fuel cells technology, which requires hydrogen sulfide-free feed gas. This led to review papers addressing this topic from various angles. Examples are the reviews focused exclusively on a broad range of technologies including biological treatment (scrubbers, filters), absorption (in solutions of amines, ionic liquids, deep eutectic solvents, hybrid blends), adsorption (on zeolites, metal oxides, carbon-based solvents, metal organic frameworks), electrochemical processes, and various membranes [196,197]. Another direction of the reviews' attentions is that addressing a range of materials used for the effective H_2S removal [3,15, 150,196,198,199], or focused mainly on one groups of materials [16,46, 200] or specific desulfurization needs, such as biogas purification [19] or fuel cell requirements [198]. In the specific category of carbon-based materials, a recent review addressed a specific methodology of enrichment of the carbon desulfurization activity by the addition of an inorganic active phase with emphasis on synergistic effects provided by both composite components [100].

In our view, this work differs from those recently published summaries in both, its organization and content. Here, we have focused on H_2S room temperature catalytic oxidation on carbonaceous materials and in the first part we addressed all factors governing and influencing that complex catalytic behavior. Many findings on H_2S room temperature oxidation have been published decades ago and we consider them as still valid and influential. Nevertheless, aware of recent developments in science, and based on the interconnection of factors, we have added the critical comments on those findings and/or proposed alternative or deeper explanations. We consider the first part of this review as a very important one not only to understand the target catalytic process but also to form a solid base intended to inform further advancements in this field. The recent developments in H_2S catalytic oxidation on carbon-based materials consist of the second parts of this review. There we showed the examples of research approaches where all mentioned at the beginning factors influencing H_2S catalytic oxidation were taken into account to achieve the unprecedented performance of carbon-based catalysts in room temperature H_2S oxidation.

As the collected results indicated, the virgin carbon materials have a low activity in H_2S catalytic oxidation, and to improve their H_2S removal efficiency, various modifications are necessary, such as an alkaline species deposition, heteroatoms doping as well as metal oxides loading. While the nitrogen heteroatoms themselves have no direct reactivity towards H_2S , they provide a basic environment for H_2S dissociation. Similar role is assigned to alkaline earth oxides. On the other hand, transition metal oxides might work as redox catalysts, as iron oxides do, provide synergistic effect owing to enhancing an electron transfer between the carbon matrix and metal oxides, or directly activating oxygen as copper oxide and metallic copper nanoparticles do. The oxygen activation process leading to O^* or/and $O_2^{\cdot-}$ is very important for catalytic oxidation and here, micropores of carbons, due to strong oxygen adsorption forces play a vital role. Nitrogen species doped to the carbon matrix also contribute to this process.

Different modification strategies would result in remarkable differences in the extent of H_2S catalytic oxidation. We have shown that due to the differences in the morphology, dimensions, porous structure, graphitization degree, conductivity as well as surface chemistry, the H_2S removal efficiency might differ markedly even when the same modification strategy but on different carbon materials has been adopted. Recent years, although they have brought great achievements in H_2S catalytic oxidation on the carbon materials at room temperature, they still left some challenges to be addressed.

Although the alkaline modification is a highly efficient strategy for improving the H_2S catalytic oxidation performance on the carbon materials, it might result in a low self-ignition temperature of carbon owing to highly exothermic acid-base reactions plus it might lead to equipment

corrosion. Even though nitrogen-doped carbons as metal-free catalysts can be considered as feasible alternatives, and recent results certainly showed their very promising activity, their preparation, especially with the high pyridine nitrogen content and high volume of mesopores storing sulfur, still remains a challenge. Moreover, some catalysts which provide a basic environment cannot be used for desulfurization of digester gas where a high content of reactive CO₂ renders their catalytic activity.

Oxygen activation on the carbon materials is very important for catalytic oxidation of H₂S and micropores, especially the ultramicropores with sizes below 0.7 nm are considered as the active centers for this process owing to their high adsorption potential and space confinement effect. Nevertheless, in spite of a small volume of micropores, mesoporous carbon materials modified with nitrogen, exhibit the excellent H₂S catalytic oxidation performance, even higher than that on carbons enriched in micropores. This is due to the dual role of nitrogen in the carbon matrix providing not only basicity but also oxygen activating centers. Therefore, the oxygen activation process on the carbon materials should be further explored, with more attention directed to combine the effect of ultramicropores to that of the heteroatom-based interface, which is formed by strong interactions between carbon materials and the deposited species. Another feature to be optimized is the electron transfer efficiency which is important for both oxygen activation and H₂S oxidation in redox reactions. The combination of micro- and mesopores needs optimization and it is especially important for direct desulfurization of digester gas in the absence of air, where micropores with adsorbed oxygen can play a vital role in a O₂ supply, activation and thus in H₂S oxidation.

Another aspect to explore is autocatalysis of H₂S oxidation by sulfur or the role of surface hydrophobicity and water in the sulfur transport in the pore system. Even though those mechanisms have been hypothesized, the sound explanations of these processes need further elaboration.

Besides the H₂S removal performance, another important evaluation index for the catalysts is their cost. Activated carbon-based catalysts are inexpensive, but their developed microporosities and limited mesopores restrict the desulfurization efficiency. Although carbon nanotubes, graphite/graphene oxides and carbon nanofibers-based catalysts exhibit the excellent H₂S removal performance, their relatively high costs impede their applications. Mesoporous carbons, especially prepared from biomass or/and solid waste show great potential in this respect, and more work should be devoted to them towards an advancement in the inexpensive methods of a mesopore development.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

This is the review paper. The data is taken for other works with permissions.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (Grant No. 21576180, Grant No. 21878209 and Grant No. 22208233) and Fundamental Research Program of Shanxi Province (No. 20210302123065, No. 202203021211140).

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